

Petrology of the Meade Peak Phosphatic  
Shale Member of the Phosphoria  
Formation at Coal Canyon, Wyoming  
*and*

A Method of X-Ray Analysis for  
Determining the Ratio of Calcite to  
Dolomite in Mineral Mixtures

---

GEOLOGICAL SURVEY BULLETIN 1111-C,D

*Prepared partly on behalf of the U.S.  
Atomic Energy Commission and  
published with the permission  
of the Commission*





Petrology of the Meade Peak Phosphatic  
Shale Member of the Phosphoria  
Formation at Coal Canyon, Wyoming

*and*

A Method of X-Ray Analysis for  
Determining the Ratio of Calcite to  
Dolomite in Mineral Mixtures

By R. A. GULBRANDSEN

CONTRIBUTIONS TO GENERAL GEOLOGY

---

GEOLOGICAL SURVEY BULLETIN 1111-C, D

*Prepared partly on behalf of the U.S.  
Atomic Energy Commission and  
published with the permission  
of the Commission*



**UNITED STATES DEPARTMENT OF THE INTERIOR**

**FRED A. SEATON, *Secretary***

**GEOLOGICAL SURVEY**

**Thomas B. Nolan, *Director***

## CONTENTS

---

	Page
(C) Petrology of the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyoming, by R. A. Gulbrandsen.	71
(D) A method of X-ray analysis for determining the ratio of calcite to dolomite in mineral mixtures, by R. A. Gulbrandsen.-----	147



# Petrology of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation at Coal Canyon, Wyoming

*By* R. A. GULBRANDSEN

CONTRIBUTIONS TO GENERAL GEOLOGY

---

GEOLOGICAL SURVEY BULLETIN 1111-C





# CONTENTS

---

	<b>Page</b>
Abstract.....	71
Introduction.....	72
Acknowledgments.....	74
Coal Canyon section of the Phosphoria formation.....	74
Meade Peak phosphatic shale member.....	76
Methods of study.....	76
Chemical composition.....	76
Major constituents.....	76
Averages and comparisons.....	80
Minor constituents.....	82
Elements determined by spectrographic analyses.....	82
Element relationships in the vanadiferous zone.....	84
Selenium.....	85
Uranium.....	86
Mineral composition.....	86
Mineral-norm calculations.....	87
Comparison of percentage ratios of calcite to dolomite.....	89
Mineralogy.....	91
Carbonate minerals.....	91
Diadochy in dolomite and calcite.....	91
Carbonate-fluorapatite.....	98
Relation to the apatite mineral group.....	99
Diadochy in the carbonate-fluorapatite of the Meade Peak member.....	101
Phosphate mineral name.....	104
Submicrocrystalline character of carbonate-fluorapatite.....	105
Feldspar.....	105
Quartz and microcrystalline quartz.....	110
Mica group.....	111
Kaolin group.....	112
Iron sulfides.....	113
Iron oxides.....	113
Other sulfur compounds.....	114
Carbonaceous material.....	114
Accessory minerals.....	114
Petrography.....	114
Rock types.....	114
Composition.....	115
Range of mixtures of end-member rock types.....	115

Petrography—Continued	Page
Carbonate rock.....	116
Petrographic types of carbonate.....	116
Texture.....	117
Inclusions.....	118
Replacement.....	118
Cleavage and twinning.....	119
Phosphorite.....	119
Petrographic types of carbonate-fluorapatite.....	119
Texture.....	119
Inclusions and color.....	120
Development of pellets and oolites.....	120
Quartz-silicate rock.....	121
Petrology.....	122
Nature of rock-type changes.....	122
Range and distribution of the calcium.....	123
Mixtures of apatite, dolomite, and calcite.....	123
Broader relationships of mineral associations.....	125
Formation of dolomite, calcite, and carbonate-fluorapatite.....	126
Requirement of circulating sea water.....	127
Role of organisms.....	127
Dolomite-calcite-carbonate-fluorapatite-sea water system.....	128
Solubility of calcite.....	129
Solubility of dolomite.....	130
Solubility of carbonate-fluorapatite.....	131
Explanation of phase relations.....	132
Phase relations in the rocks of the Meade Peak phosphatic shale member.....	133
Conclusions.....	134
References cited.....	139
Index.....	145

---

## ILLUSTRATIONS

---

[Plates 28 and 29 in pocket]

- PLATE 28.** Columnar section of the Meade Peak phosphatic shale member.
29. Spectrographic data of the minor elements in the Meade Peak phosphatic shale member.
30. *A*, Quartz crystal in vein in carbonate rock. *B*, Bent muscovite in carbonate rock..... Facing 124
31. *A*, Granular texture of carbonate rock. *B*, Euhedral dolomite phenocryst set in a fine-grained matrix..... Following 124
32. *A*, Subhedral dolomite crystals showing mutual interference in their growth. *B*, Carbonate-fluorapatite crystal... Following 124
33. *A*, Apatite pellets in phosphorite. *B*, Apatite oolites in phosphorite..... Facing 125

	Page
FIGURE 4. Index map showing approximate extent of the western phosphate field and location of the stratigraphic section of the Meade Peak phosphatic shale member at Coal Canyon.....	73
5. Generalized section of the Phosphoria formation at Coal Canyon.....	75
6. Graph showing X-ray measurement of diadochy in calcite and dolomite.....	93
7. Graph showing relation of X-ray peak position to composition of some carbonate minerals.....	96
8. Graph showing partial X-ray patterns of albite, orthoclase, and mixtures of the two.....	107
9. Graph showing partial X-ray patterns of orthoclase and sanidine.....	108
10. Ternary plot of principal mineral components.....	116
11. Graph showing frequency of occurrence of percentages of CaO.....	124
12. Ternary plot of the percentages of calcite, dolomite, and carbonate-fluorapatite.....	125
13. Diagram showing formation of dolomite, carbonate-fluorapatite, and calcite by evaporation.....	135
14. Diagram showing formation of dolomite, carbonate-fluorapatite, or calcite by increase in concentration of one component.....	137

---

## TABLES

---

TABLE 1. Chemical analyses, in percent by weight, of rocks of the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyo.....	77
2. Average chemical composition, in percent by weight, of end-member types (15 samples of each type) and of the Meade Peak phosphatic shale member.....	80
3. Comparison of ratios of constituents in end-member rock types and the Meade Peak phosphatic shale member with other shale and limestone averages.....	81
4. Occurrence of minor elements in the end-member rock types.....	83
5. Chemical analyses of selenium in samples from parts of the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyo.....	85
6. Mineral norms, in percent by weight, for carbonate-fluorapatite, dolomite, and calcite in the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyo.....	88
7. Comparison of percentage ratio of calcite to dolomite as determined by using two independent methods.....	90
8. Spectrographic analyses, in percent, of dolomite and calcite standards.....	94

	Page
TABLE 9. Comparison of the mean difference between the most intense X-ray peaks of calcite and dolomite and quartz in carbonate rocks and in prepared mineral mixtures.....	95
10. Diadochy in some minerals of the apatite group.....	99
11. Ionic radii (sixfold coordination) and radius ratios of ions in apatite.....	100
12. Coordination of cations.....	100
13. Comparison of the percentages of $\text{Na}_2\text{O}$ , $\text{SO}_3$ , and $\text{V}_2\text{O}_5$ in phosphorite with that in carbonate and quartz-silicate rocks....	102
14. Comparison of the mean percentages of $\text{Na}_2\text{O}$ , $\text{SO}_3$ , and $\text{V}_2\text{O}_5$ in carbonate and quartz-silicate rocks with that in phosphorite, as determined by modified <i>t</i> tests.....	103

## CONTRIBUTIONS TO GENERAL GEOLOGY

---

### PETROLOGY OF THE MEADE PEAK PHOSPHATIC SHALE MEMBER OF THE PHOSPHORIA FORMATION AT COAL CANYON, WYOMING

---

By R. A. GULBRANDSEN

---

#### ABSTRACT

The Coal Canyon, western Wyoming, section of the Meade Peak phosphatic shale member of the Phosphoria formation is located about 20 miles southeast of the type locality of the Meade Peak member and within the region in which the Meade Peak is characteristically developed. The member is 143 feet thick at Coal Canyon and consists of dark thin-bedded phosphorites and carbonate and quartz-silicate rocks. The rocks of the section have been studied in detail with particular emphasis upon the characteristics of the phosphorites and carbonate rocks and their modes of formation.

The average chemical composition, in percent, of the member is:  $\text{SiO}_2$ , 26.5;  $\text{TiO}_2$ , 0.2;  $\text{Al}_2\text{O}_3$ , 4.5;  $\text{Fe}_2\text{O}_3$ , 1.8;  $\text{MgO}$ , 4.5;  $\text{CaO}$ , 27.0;  $\text{Na}_2\text{O}$ , 0.9;  $\text{K}_2\text{O}$ , 1.6;  $\text{P}_2\text{O}_5$ , 10.6;  $\text{CO}_2$ , 13.8; F, 1.1;  $\text{SO}_3$ , 2.0;  $\text{H}_2\text{O}$ , 0.9; and carbonaceous material, 4.8. This "average" rock contains unusually high amounts of phosphorus and fluorine. The average calcium-magnesium ratio for the member is 6, but it ranges from 88 for the average phosphorite to 2.9 for the average carbonate rock.

Important minor constituents that occur in the rocks in significant amounts are vanadium, selenium, and uranium. In 3.5 feet of carbonaceous quartz-silicate rock, the vanadiferous zone, vanadium averages 0.7 percent  $\text{V}_2\text{O}_5$  and selenium content ranges from 90 to 150 ppm. The uranium content of the whole member ranges from 0.0005 to 0.034 percent and averages 0.004 percent. The higher uranium contents are in phosphorites.

Dolomite makes up 21 percent of the member and calcite, 8 percent. Both minerals contain only small amounts of cation substitutes, as indicated by the position of X-ray diffraction peaks. The principal ion diadochie for calcium in calcite is magnesium, and the principal ion diadochie for magnesium is calcium. Ratios of calcite to dolomite in the carbonate rocks of the member, as determined by an X-ray method, compare favorably with ratios calculated from chemical analyses.

Carbonate-fluorapatite makes up 28 percent of the member. Small amounts of ionic substitution in the mineral are indicated—sodium, strontium, and uranium for calcium; sulfur and silicon for phosphorus; and possibly some fluorine for oxygen.

The quartz-silicate group of minerals makes up 33 percent of the member and comprises quartz and microcrystalline quartz, orthoclase, microcline, albite,

muscovite, biotite, illite, kaolinite, titanite, zircon, and tourmaline. The principal kinds of feldspar, orthoclase and albite, were identified by X-ray analysis. Illite-muscovite, also determined by X-ray analysis, is more abundant than kaolinite.

The three principal compositional rock types are characterized by the dominance of a mineral or mineral group: carbonate-fluorapatite in phosphorite, calcite and dolomite in carbonate rock, and the quartz-silicate group of minerals in quartz-silicate rock. Most of the rocks are composed of silt-size particles, but many phosphorites are composed of pellets and oolites of sand size. The rock strata most commonly consist of beds 0.5 to 2 feet in thickness and occur in unsystematic alternation of one upon another. There is no favored pair of rock types or sequence of the three types.

Carbonate-fluorapatite, dolomite, and calcite, chemically related compounds that have calcium and carbonate ions in common, occur in the rocks of the member in three principal associations: carbonate-fluorapatite alone, dolomite-carbonate-fluorapatite mixtures, and dolomite-calcite mixtures. As a basic hypothesis, these occurrences are considered to represent approximately the solid phase or phases of these minerals in equilibrium with the sea water from which they formed. Where found alone, carbonate-fluorapatite represents a first-stage differentiation of sea water by evaporation, or a precipitation owing to a sustained addition of phosphate to sea water by the dissolution of dead organisms, for example. The dolomite-carbonate-fluorapatite mixtures represent a second-stage differentiation, following the precipitation of apatite alone, in which the two minerals form together in proportions high in dolomite. These two closely related kinds of mineral associations are dominant in the Coal Canyon section. The dolomite-calcite mixtures cover a wide range of proportions that is not readily explained in terms of simple phase relations. Under conditions in which dolomite is the single solid phase in equilibrium with sea water, however, calcite could precipitate metastably and change with time, while in contact with sea water, to dolomite. In this manner, the amount of dolomite formed is a function of the time during which calcite is in free contact with sea water, and all proportions of dolomite and calcite are possible.

## INTRODUCTION

Phosphorites of the Phosphoria formation of Permian age are among the largest and most widely known phosphate deposits in the world and make up a major part of the phosphate resources of the United States. The formation also contains large potentially valuable amounts of minor elements. Because of the present and future economic importance of these deposits, the U.S. Geological Survey has undertaken on behalf of the Division of Raw Materials of the U.S. Atomic Energy Commission an extensive detailed study in the region composed of southwestern Montana, southeastern and south-central Idaho, western Wyoming, northern Utah, and northeastern Nevada (see fig. 4). The present study, which is only one aspect of the broad program, concerns the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyo., in regards to element, mineral, and rock composition, and the relationships among the constituents. These data bear on many problems of geology, but it has been possible to treat in some detail, only a few here. Emphasis

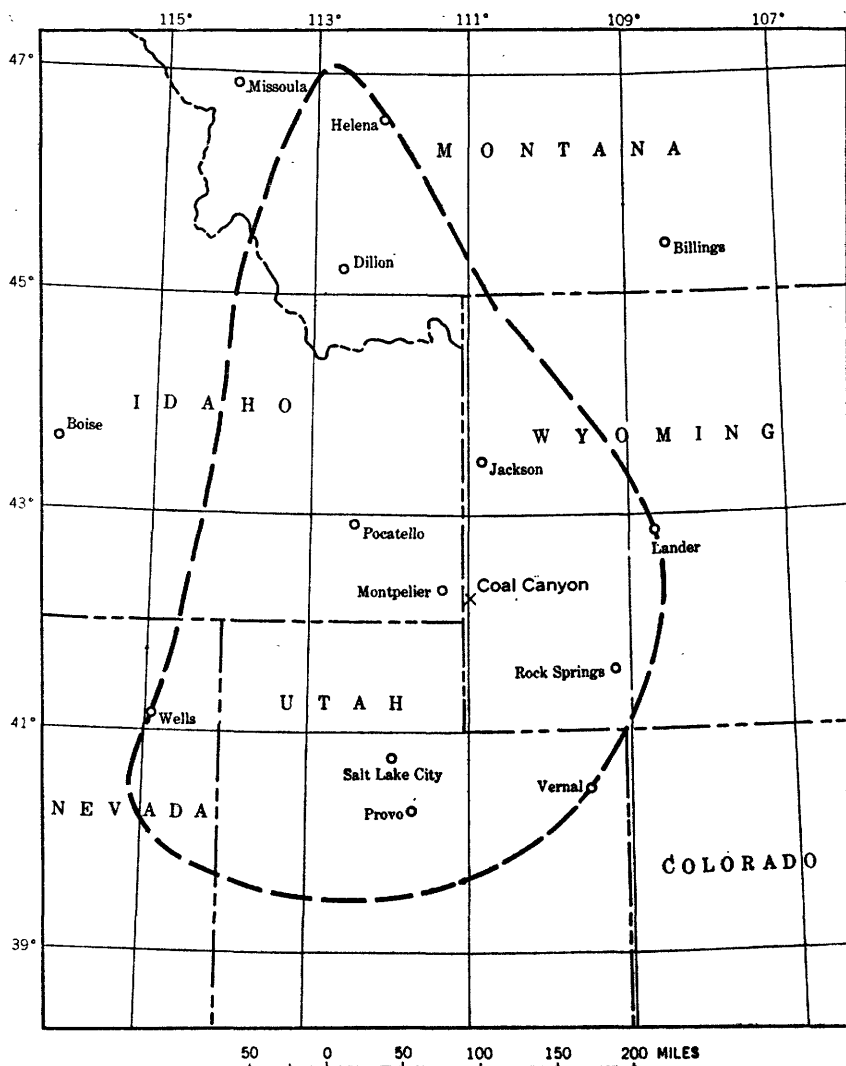


FIGURE 4.—Index map showing approximate extent of the western phosphate field and location of the stratigraphic section of the Meade Peak phosphatic shale member at Coal Canyon.

is placed on the characteristics of the phosphorites and associated carbonate rocks, and some hypotheses regarding the mode of formation of these rocks are presented.

The stratigraphy of the Phosphoria formation has been described recently by McKelvey and others (1956). Various aspects of the petrography and petrology of the formation have been treated by Mansfield (1927), Keller (1941), McKelvey (1946), Lowell (1952), McKelvey, Swanson, and Sheldon (1953), Thompson (1953, 1954),

Cressman (1955), Herr,<sup>1</sup> Weaver (1955), Emigh (1958), McKelvey and Carswell (1956), Rooney,<sup>2</sup> and Sheldon (1957).

#### ACKNOWLEDGMENTS

This study was suggested by V. E. McKelvey, and his continued interest in and suggestions about the work are greatly appreciated. The work has benefited from my discussions with other colleagues, particularly E. R. Cressman, R. P. Sheldon, and T. M. Cheney, who have worked or are currently working on related aspects of the phosphate deposits. A critical review of the manuscript by K. B. Krauskopf has been especially helpful. J. P. Miller kindly furnished the optical-grade calcite used as reference material in some of the experimental work.

#### COAL CANYON SECTION OF THE PHOSPHORIA FORMATION

The Coal Canyon section of the Phosphoria formation is in sec. 7, T. 26 N., R. 119 W., Lincoln County, Wyo. (fig. 4). A trench exposing the formation, where not naturally exposed, is on the south side of the canyon on the steeply dipping east limb of the Sublette anticline. The section was measured and described by V. E. McKelvey, L. E. Smith, and D. M. Larrabee, and sampled by R. A. Gulbrandsen. Chemical and spectrographic analyses, accompanied by a brief description of the units, are included in a compilation of stratigraphic sections of the Phosphoria formation by McKelvey and others (1953).

Coal Canyon is about 20 miles southeast of the type section of the Phosphoria at Phosphoria Gulch, Idaho, described by Richards and Mansfield (1912), and lies near the east margin of the region in which the Phosphoria is typically developed. McKelvey and others (1956), on the basis of detailed stratigraphic studies, recognize six members of the formation, and reference should be made to their work for descriptions of the units and their regional relationships. The members present at Coal Canyon are, from the base upwards, the Mead Peak phosphatic shale member, the Rex chert member, and the Retort phosphatic shale member. A generalized section at Coal Canyon is presented in figure 5. The Meade Peak member is composed of 144 feet of interbedded soft to hard fissile to thick-bedded dark gray phosphorite, carbonate rock, and mudstone. The Rex chert member, 67 feet thick, consists of gray hard massive chert and a small amount of gray limestone randomly distributed in the chert as

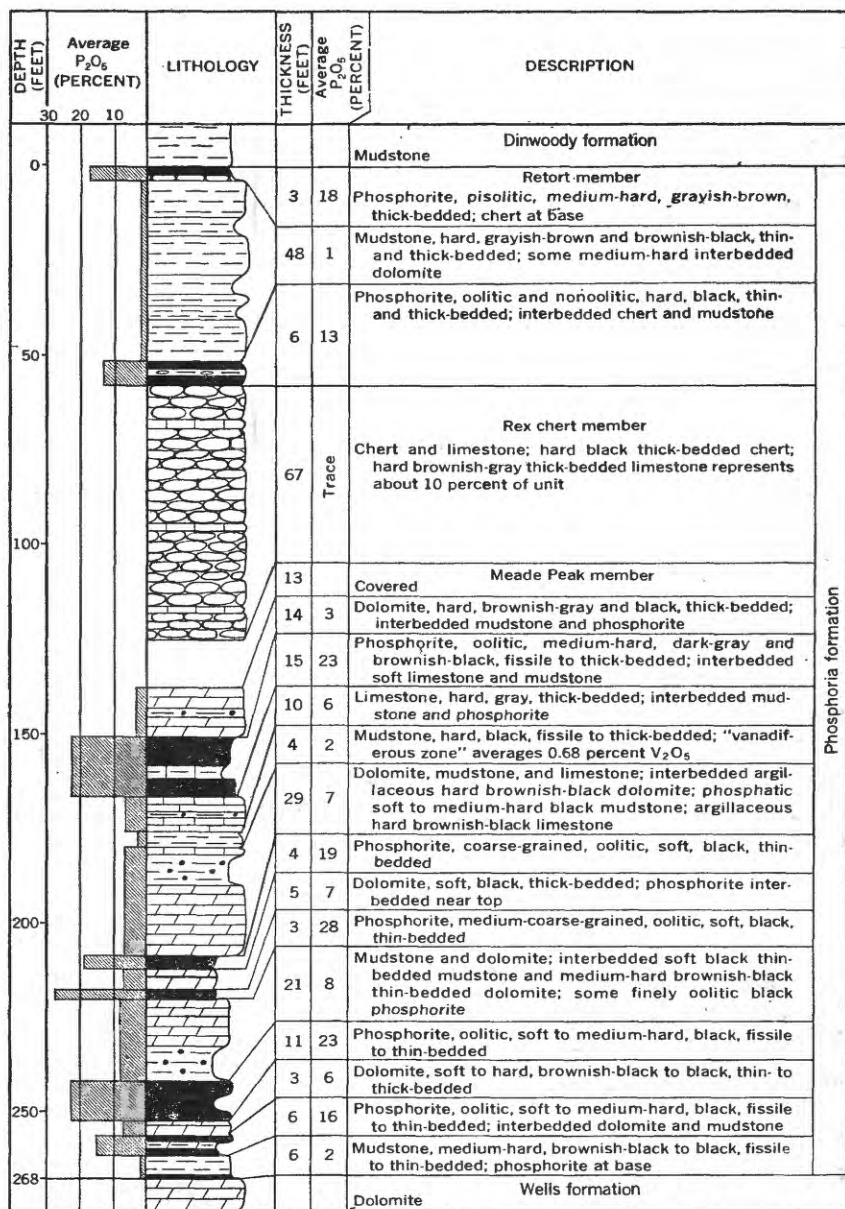
---

<sup>1</sup> Herr, G. A., 1955, Clay minerals in the Phosphoria formation in Beaverhead County, Montana: Indiana Univ. thesis.

<sup>2</sup> Rooney, L. F., 1956, A stratigraphic study of the Permian formations of part of southwestern Montana: Indiana Univ. thesis.



irregularly shaped nodules and lenses. The Retort member, 57 feet thick, is composed mostly of thin-bedded hard brownish-black mudstone and phosphorite with minor amounts of chert, and it is similar to the Meade Peak member in general character.



From McKelvey, Smith, Hoppin, and Armstrong (1953)

FIGURE 5.—Generalized section of the Phosphoria formation at Coal Canyon.

### MEADE PEAK PHOSPHATIC SHALE MEMBER

The Meade Peak phosphatic shale member is the economically important member of the Phosphoria formation in the southeastern Idaho-western Wyoming-northern Utah area. The Coal Canyon section lies within this area, and the member has been studied at this locality to obtain detailed information about the lithologic character of the rocks, their associations, and factors relating to their origin.

A detailed columnar section of the member is presented in plate 28. It shows graphically: color, grain size, rock composition, thickness of bedding, mineral composition, structure, and special features of the rocks. Color was determined on crushed-rock samples by comparison with a color chart based on the color-solid dimensions of the Munsell system (Goddard and others, 1948); for example, bed P-50 is brownish black, which is hue 5 yellow-red of chroma 1 and value 3, or notation 5 YR 3/1 on the Munsell chart. The procedure for calculating the mineral norms in the rock-composition column is described on p. 87.

### METHODS OF STUDY

Fine-grained rocks, such as those considered in this report, are difficult to study and require complementary analytical methods for the determination of even a minimum of rock characteristics. Thin-section, X-ray, chemical, and spectrographic methods were used. Thin sections were used for mineral identification and for the study of texture and mineral relationships. X-ray analysis was used for mineral identification, a study of diadochy in the carbonate minerals, the calculation of calcite-dolomite ratios, and differentiation of feldspar types. Chemical and spectrographic analysis was used to determine rock composition and geochemical relationships, for the calculation of mineral norms, and for the study of diadochy in carbonate-fluorapatite and the carbonate minerals.

### CHEMICAL COMPOSITION

#### MAJOR CONSTITUENTS

Chemical determination of 16 constituents have been made of all but 2 beds of the section by the Tennessee Valley Authority (table 1). The analyses were made on splits of channel samples collected from each bed, giving in effect a complete analysis of all the rocks of the section. The chemical analyses serve as the basic data for calculating mineral and mineral group norms and for determining the geochemical relationships of the elements.

Quantitative chemical analysis of rocks of the Phosphoria is complex and difficult. The accuracy of the analyses is not known, but some

TABLE 1.—Chemical analyses, in percent by weight, of rocks of the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyo.

[A.I., acid-insoluble; L.O.I., loss on ignition; eU, equivalent uranium as determined by radioactivity analyses U.S. Geological Survey; U, uranium as determined by chemical analyses, U.S. Geological Survey. Chemical analyses, with exception of uranium, by the Tennessee Valley Authority under the direction of J. H. Walshall (McKelvey and others, 1953)]

Bed	CaO	MgO	CO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	F	S as SO <sub>2</sub>	H <sub>2</sub> O—	A.I.	L.O.I.	eU	U
P-107	29.80	11.1	33.8	0.76	17.58	2.5	0.9	0.54	0.63	0.14	0.04	0.13	0.51	0.26	20.0	35.7	0.0005	0.001
106	39.40	14.7	2.6	25.45	17.80	4.1	1.5	1.35	1.50	0.05	0.05	2.5	2.3	0.67	17.8	6.2	.005	.003
105	5.60	.82	8	3.25	61.52	13.3	4.0	1.35	3.90	0.01?	0.07	0.37	.80	1.02	75.6	5.9	.002	.002
104	9.00	.67	.8	6.15	57.58	10.9	3.1	.59	3.30	.47	.06	.59	.91	1.02	68.8	6.3	.004	.002
103	6.00	.63	.6	4.35	61.14	12.1	3.4	.40	3.57	.45	.04	.48	.76	1.04	73.3	6.3	.003	.001
102	9.00	.65	10.4	6.65	55.26	9.3	3.0	.84	2.53	.54	.02	.15	.31	.43	69.3	7.7	.002	.001
101	10.40	.90	3.2	4.51	57.11	10.2	3.3	1.02	1.67	.43	.04	.52	.77	.63	69.3	6.5	.002	.001
100	40.80	.39	3.8	25.9	17.70	3.6	1.1	1.09	1.80	.17	.04	2.4	2.0	.62	19.0	7.7	.005	.003
99	22.20	10.0	26.6	.81	30.02	4.3	1.5	1.00	1.22	.31	.06	.15	.48	.31	35.6	28.3	.001	.001
98	46.2	.24	4.4	29.8	9.91	1.4	.8	.83	.60	.09	.07	.31	2.3	.50	8.2	6.2	.009	.008
97	49.1	.20	2.0	32.9	4.73	.9	.6	1.01	1.10	.16	.10	3.8	2.9	.46	3.2	5.4	.022	.021
96	39.8	.37	1.7	27.2	13.87	2.3	1.1	1.76	1.10	.16	.23	2.9	2.9	1.47	12.4	8.6	.034	.034
95	44.1	.34	2.3	29.8	8.85	1.5	1.7	1.03	.92	.12	.28	3.1	3.2	1.26	7.2	8.0	.026	.028
94	39.7	.36	1.9	26.9	13.28	2.1	1.0	.91	.92	.12	.24	2.7	4.0	1.73	11.4	9.6	.018	.019
93	45.7	.24	2.2	32.7	6.49	1.2	.5	1.16	.54	.05	.15	3.4	3.5	1.02	5.2	6.9	.019	.019
92	32.40	.39	1.3	21.6	27.10	4.2	1.7	1.20	1.80	.26	.16	2.2	2.8	1.12	22.2	9.0	.017	.008
91	12.80	3.8	8.8	3.80	47.36	7.8	2.6	.96	2.30	.42	.08	.51	1.1	.83	58.5	13.5	.004	.001
90	25.60	4.9	24.8	.20	32.32	3.4	2.0	.90	1.47	.01?	.11	.12	.85	.32	38.6	26.6	.001	.002
89	42.24	.33	1.6	29.3	12.90	2.0	2.3	1.00	.77	.14	.10	3.0	3.2	.89	10.6	9.5	.009	.007
88	48.42	.41	11.8	24.09	6.70	.8	.8	1.14	.45	.08	.06	2.6	2.3	.56	4.7	15.0	.005	.003
87	31.46	.42	1.8	21.03	27.70	4.4	1.6	1.09	1.24	.32	.11	1.9	2.5	.87	29.2	8.3	.007	.003
86	41.60	.31	2.1	27.45	15.50	2.1	1.2	1.25	.70	.16	.06	2.9	2.9	.89	13.9	8.1	.007	.005
85	44.18	.29	4.7	27.44	14.10	1.4	1.1	1.20	.40	.16	.04	3.0	2.3	.58	11.3	8.1	.005	.004
84	25.41	.43	2.0	16.52	34.24	5.3	1.9	1.09	1.60	.40	.05	1.6	2.4	1.08	40.4	9.5	.012	.012
83	44.00	.26	2.3	29.41	13.20	2.3	1.7	.94	1.62	.15	.05	3.2	1.6	.47	11.80	5.4	.009	.006
82	26.80	2.1	20.8	2.11	35.27	5.8	2.1	.74	1.45	.19	.06	.24	.90	.34	41.2	22.1	.002	.006
81	13.40	4.2	10.0	4.04	47.21	8.8	2.5	.84	2.43	.42	.05	.45	.90	.84	56.8	14.2	.003	.001
80	28.4	.80	9.6	9.90	31.21	6.7	2.3	.45	1.89	.32	.09	1.1	2.1	1.35	37.0	16.8	.006	.003
79	15.40	2.21	10.5	2.16	47.41	9.7	3.0	.62	2.45	.10	.05	.31	3.0	.86	54.7	16.5	.003	.000
78	42.10	.43	1.9	28.67	7.70	1.9	2.1	.90	.67	.14	.11	2.8	3.5	1.55	6.62	13.1	.006	.004
77	30.80	1.70	14.0	9.92	21.10	6.2	2.6	1.00	1.49	.26	.07	1.1	2.2	1.37	25.2	22.0	.003	.003
76	1.8	.06	40.2	.36	4.82	1.1	5	.5	1.72	.03	.06	.06	.44	.13	5.90	41.1	.004	.001
75	6.05	2.3	6.9	2.73	47.18	8.6	3.4	1.25	2.12	.62	.52	.44	8.6	.51	59.30	16.7	.006	.002
74	8.05	2.3	5.0	.34	41.64	9.8	3.9	.78	2.55	.18	1.75	.15	12.5	.83	51.2	24.9	.005	.002
73	4.20	2.7	6.1	.20	45.64	9.6	4.0	.99	2.78	.23	1.45	.23	10.5	.62	66.38	16.6	.003	.001
72	13.60	1.4	5.6	.05	52.58	9.7	4.4	1.30	2.85	.36	.37	.08	8.6	.32	68.75	17.4	.003	.006
71	36.40	1.8	29.3	6.30	37.36	7.1	3.3	1.17	2.11	.26	.14	.67	9.4	.37	46.66	30.7	.004	.002
70	36.40	1.8	29.3	8.31	22.98	2.6	1.2	1.10	2.70	.08	.06	.10	.60	.29	27.6	10.3	.004	.005
69	13.20	.53	5.1	8.31	45.07	9.3	2.6	1.30	2.38	.43	.08	.08	1.6	1.33	57.9	11.3	.004	.002
68	5.40	2.4	5.1	.76	59.80	9.2	3.8	1.50	2.30	.42	.08	.09	.90	.99	73.0	11.3	.002	.005



24	42.3	.60	3.3	28.6	11.63	1.4	.7	.90	.88	.10	.09	2.6	2.8	10.5	7.8	.010
23	41.2	.80	3.6	26.7	13.36	1.9	.8	.95	1.07	.12	.14	2.7	3.1	12.3	9.1	.013
22	35.4	2.2	6.4	21.1	18.16	2.0	1.0	.88	1.51	.16	.10	2.1	3.1	18.5	12.2	.010
21	30.4	3.7	9.8	16.4	22.77	2.2	1.3	.70	1.88	.21	.09	1.8	3.1	14.7	14.7	.010
20	27.8	5.0	12.5	12.8	25.87	2.8	1.4	.60	1.53	.08	.03	1.4	2.1	28.0	17.1	.004
19	29.4	3.3	8.6	15.5	25.91	2.7	1.3	.63	2.26	.21	.06	1.7	2.3	27.3	14.0	.006
18	26.7	9.0	23.5	6.9	21.20	2.0	1.2	.30	2.29	.11	.06	1.6	1.1	23.8	26.5	.002
17	30.9	5.9	16.0	13.3	21.25	1.7	1.1	.42	1.65	.31	.05	1.6	1.5	16.1	19.0	.004
16	28.2	12.2	33.2	5.2	16.21	1.2	1.5	.33	1.79	.09	.05	1.6	1.0	16.1	32.6	.002
15	36.40	2.4	7.1	21.55	16.64	3.1	1.3	.83	1.52	.15	.05	2.5	2.6	18.5	11.9	.004
14	30.60	12.3	29.8	6.4	15.20	1.5	1.8	.40	1.78	.08	.05	1.6	1.1	16.5	31.7	.001
13	35.00	6.7	17.7	11.5	16.02	1.2	1.5	.77	.83	.17	.05	1.3	1.2	16.2	20.2	.002
12	32.15	10.1	25.3	11.5	13.00	1.2	1.7	.62	.69	.12	.05	1.6	1.2	12.2	27.3	.003
11	43.82	.6	3.7	28.9	10.09	1.1	.7	1.09	.45	.16	.11	3.4	3.5	7.9	9.1	.013
10	16.82	3.7	8.0	7.5	39.08	5.6	2.7	.45	2.25	.24	.09	.91	2.8	44.0	18.3	.005
9	26.8	9.5	21.9	9.7	17.98	2.4	1.4	.42	1.31	.14	.09	.93	2.1	20.0	25.6	.002
8	31.1	.57	1.9	20.6	26.27	3.2	1.6	.79	1.58	.19	.17	2.2	3.7	26.4	9.0	.007
7	9.1	.80	6.1	5.0	55.29	4.2	3.4	.59	3.96	.45	.36	.77	3.1	62.7	11.5	.005
6	10.00	5.8	13.3	5.0	53.36	7.5	2.5	.40	4.10	.18	.09	.12	3.1	64.7	14.9	.003
5	4.96	3.0	6.1	.3	61.56	9.7	3.1	.17	4.10	.16	.04	.19	1.5	73.5	10.7	.001
4	7.28	.87	.3	.44	61.56	9.8	4.6	.24	5.03	.11	.19	.29	3.7	74.7	12.8	.001
3	2.60	.72	.3	.10	71.04	8.8	3.7	.80	5.07	.10	.11	.23	1.6	81.5	6.6	.001
2	1.4	1.9	2.3	.67	68.28	10.1	3.1	.85	4.50	.18	.08	.25	1.1	80.3	6.5	.003
1	42.24	1.9	5.1	29.05	10.20	2.5	.7	.95	.40	.70	.10	2.9	2.2	8.3	7.4	.005

measure of precision is obtained from a few duplicate analyses. For these the mean deviation ranges from about 0.5 to 1.5 percent for a few constituents. Percentage error (mean deviation divided by the average amount of the constituent) is greatest for those constituents in small amount and is as much as 50 percent. In general, however, the precision is sufficient for most purposes for constituents present in large amount. The overall precision is not sufficient for the calculation of silicate-mineral norms, yet the mineral-norm calculations for carbonate-fluorapatite, calcite, and dolomite are the best quantitative estimates that can be made for these minerals. Comparisons of the constituents among individual beds are hazardous, but the comparisons of averages of groups of beds are very useful.

#### AVERAGES AND COMPARISONS

The average chemical composition of the Meade Peak member (table 2) is unique among stratigraphic units for which chemical data are known because of its high phosphorus (about 11 percent  $P_2O_5$ ) and fluorine (about 1 percent) content. Calcium and silica are present in about equal amount. The silica content (about 26.5 percent) is low, however, relative to its amount in many of the sedimentary rocks, which indicates the subordinate role of detrital components in the rock section. Some of the various concentrations of the constituents are shown in table 2, which compares the average values of the member with the averages of the three major end-member rock types.

TABLE 2.—Average chemical composition, in percent by weight, of end-member rock types (15 samples of each type) and of the Meade Peak phosphatic shale member

	Carbonate rock	Phosphorite	Quartz-silicate rock	Meade Peak member <sup>1</sup>
CaO-----	28.9	43.9	7.0	27.0
MgO-----	9.9	0.5	1.7	4.5
CO <sub>2</sub> -----	30.3	3.0	3.4	13.8
P <sub>2</sub> O <sub>5</sub> -----	2.6	29.5	2.6	10.6
SiO <sub>2</sub> -----	17.7	10.0	58.1	26.5
Al <sub>2</sub> O <sub>3</sub> -----	2.5	1.5	9.6	4.5
Fe <sub>2</sub> O <sub>3</sub> -----	1.1	1.0	3.4	1.8
Na <sub>2</sub> O-----	.8	1.0	.7	.9
K <sub>2</sub> O-----	.9	.6	3.4	1.6
TiO <sub>2</sub> -----	.1	.1	.4	.2
V <sub>2</sub> O <sub>5</sub> -----	.1	.1	.1	.1
F-----	.3	3.1	.4	1.1
SO <sub>3</sub> -----	1.0	2.9	2.3	2.0
H <sub>2</sub> O-----	.6	.8	1.0	.9
Carbonaceous material <sup>2</sup> -----	2.9	4.4	6.1	4.8
L.O.I. <sup>3</sup> -----	33.8	8.3	10.4	19.5

<sup>1</sup> Weighted average.

<sup>2</sup> L.O.I.—( $CO_2 + H_2O$ —).

<sup>3</sup> Loss on ignition.

The 15 analyses of each rock type used to obtain an average contained the greatest amount of the characterizing constituents—carbonate minerals, carbonate-fluorapatite, and quartz and silicate minerals. The number of samples used was largely determined arbitrarily, but an equal number of each type was selected in order to simplify statistical calculations, which are used in other kinds of comparisons described further on.

The average end-member carbonate rock is magnesium rich and contains more dolomite than calcite. The average quartz-silicate rock is more like average shale, although the amount of phosphorus is still more than 10 times greater than Clarke's (1924, p. 30) value.

The ratios of constituents, which are often more useful than absolute amounts for comparative purposes, are presented in table 3. Some of the larger differences indicate that the titanium content is low in all rocks of the Meade Peak, relative to silica, in comparison with average shale and limestone; aluminum is low, possibly iron is too, in the quartz-silicate rocks as compared with shale; magnesium is relatively very low in phosphorite and high in carbonate rock in comparison with average limestone, and low in quartz-silicate rock as compared with average shale; and sodium is high in phosphorite and carbonate rock as compared with average limestone, and low in the quartz-silicate rock as compared with shale.

TABLE 3.—Comparison of ratios of constituents in end-member rock types and the Meade Peak phosphatic shale member with other shale and limestone averages

	$\frac{\text{SiO}_2}{\text{TiO}_2}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3^1}$	$\frac{\text{CaO}}{\text{MgO}}$	$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}}$
Meade Peak member-----	130	5.9	2.4	6.0	1.8
End-member rock types:					
Carbonate rock <sup>2</sup> -----	150	7.1	2.3	2.9	1.1
Phosphorite <sup>2</sup> -----	100	6.7	1.5	88.0	.6
Quartz-silicate rock <sup>2</sup> -----	170	6.0	2.8	4.1	4.8
Average shale <sup>3</sup> -----	90	3.8	1.6	1.3	2.5
Average limestone <sup>3</sup> -----	86	6.4	1.5	5.4	6.6
Average carbonate rock of Mississippian, Pennsylvanian, and Permian ages <sup>4</sup> -----				13.5	-----

<sup>1</sup> Total Fe calculated as  $\text{Fe}_2\text{O}_3$ .

<sup>2</sup> 15 samples.

<sup>3</sup> From Clarke (1924, p. 30).

<sup>4</sup> From Chilingar (1956, p. 2257).

The significance of these variations is not clear, but the differences may reflect different conditions of origin of the rocks. The high sodium content, relative to potassium, in the carbonate rock as compared with the average limestone, for example, may indicate greater salinity, with respect to sodium, of the solution in which the carbonate minerals formed, particularly if much of the sodium occurs in occluded liquid or in substitution in the carbonate minerals.

## MINOR CONSTITUENTS

## ELEMENTS DETERMINED BY SPECTROGRAPHIC ANALYSES

Spectrographic analyses for 28 minor elements, including vanadium and titanium, which were also analyzed chemically, have been made on samples of all the beds of the section by the U.S. Bureau of Mines (McKelvey, Smith, Hoppin, and Armstrong, 1953) in Albany, Oreg. The results of these analyses are shown graphically in plate 29 in which the heavy vertical lines represent the modal class—the most frequently occurring class—for each element in the member as a whole. The blocks represent those samples whose values are above or below the modal class. Patterns within the blocks indicate the principal end-member rock type—phosphorite, carbonate rock, or quartz-silicate rock—occurring in the section. For example, bed P-34 is a phosphorite; its copper content falls in class F, one class above the modal class; the silver value falls in the modal class and so is not represented by a block, and so on.

Table 4 summarizes the spectrographic data with respect to the end-member rock types referred to previously. On the basis of the frequency of occurrence of the concentration classes with respect to the rock types, phosphorite contains concentrations, relative to one or to both of the other rock types, of silver, strontium, zinc, vanadium, and nickel(?); quartz-silicate rock contains relative concentrations of boron, titanium, zirconium, vanadium, molybdenum, manganese, and nickel; and carbonate rock contains manganese(?). Some of these relationships can be explained readily. Strontium undoubtedly occurs in the apatite of the phosphorite; titanium in titanite, zirconium in zircon, and boron in tourmaline are associated with the quartz-silicate rock components; and manganese occurs as a constituent of calcite and dolomite. The others cannot be explained so simply. McConnell (1953) believes that vanadium can occur as an ion substitute in apatite, and W. W. Rubey (McKelvey, 1946, p. 30) suggests that vanadium also occurs, in part, in a clay mineral or mica; J. Owen (written communication, 1955) and A. D. Weeks (written communication, 1956) have identified sphalerite in Meade Peak rocks at other localities, which could account for the mode of occurrence of some zinc, at least. Manganese tends to favor association with quartz-silicate rock, but the reason for this is not known. The other elements—silver, nickel, and molybdenum—are likely to be associated with the carbonaceous component of the rocks.

Krauskopf (1955, p. 422) found that silver(?), arsenic, molybdenum, nickel, lead, vanadium, zinc, and chromium are enriched in both black shales and phosphorites, and he attributes this to the carbonaceous material common to both rock types. In addition to these elements he found cobalt, rare earths, strontium, and beryllium



enriched in the phosphorites. In the Coal Canyon samples, cobalt was not detected at the sensitivity level (0.01 percent) of the method at the time of the analyses; rare earths were not determined; strontium is enriched as noted above; beryllium is of questionable enrichment, again because of the sensitivity level of the analytical method.

TABLE 4.—*Occurrence of minor elements in the end-member rock types*

[The figures represent the number of samples of each rock type falling within each concentration class.  
Concentration class: B, 0.1-1.0 percent; C, 0.01-0.1 percent; D, 0.001-0.01 percent; E, <0.001 percent;  
N, not detected]

Element	Rock types	Concentration class				
		B	C	D	E	N
Copper	Phosphorite			3	12	
	Carbonate			1	14	
	Quartz-silicate			1	14	
Silver	Phosphorite		1		14	
	Carbonate				9	6
	Quartz-silicate				8	7
Beryllium	Phosphorite				3	12
	Carbonate				1	14
	Quartz-silicate				1	14
Strontium	Phosphorite	1	10			4
	Carbonate		6			9
	Quartz-silicate		4	2		9
Barium	Phosphorite		7			8
	Carbonate		9			6
	Quartz-silicate		10			5
Zinc	Phosphorite		7	2		6
	Carbonate		2			13
	Quartz-silicate		3			12
Boron	Phosphorite		1	14		
	Carbonate		1	14		
	Quartz-silicate		13	2		
Titanium	Phosphorite		15			
	Carbonate		15			
	Quartz-silicate	10	5			
Zirconium	Phosphorite		5	10		
	Carbonate		4	11		
	Quartz-silicate		15			
Lead	Phosphorite		3			12
	Carbonate		2			13
	Quartz-silicate		2			13
Vanadium	Phosphorite	4	10	1		
	Carbonate		13	2		
	Quartz-silicate	4	10	1		
Chromium	Phosphorite	1	14			
	Carbonate		13	2		
	Quartz-silicate		13	2		
Molybdenum	Phosphorite			13		2
	Carbonate			11		4
	Quartz-silicate		5	9		1
Manganese	Phosphorite		2	11		2
	Carbonate		5	10		
	Quartz-silicate		9	6		
Nickel	Phosphorite		10	5		
	Carbonate	1	6	7		1
	Quartz-silicate		13	2		

In a study of the factors controlling concentration of rare metals in sea water, Krauskopf (1956, p. 30) found that adsorption and biologic processes are the most general controls, that sulfide formation may be of local importance for a few elements, and that one element, chromium, forms an hydroxide in a reducing environment. He determined from his experiments that adsorption of the rare metals by various materials is significant in nearly all cases, but that only copper, zinc, and lead are strongly adsorbed by all the adsorbents tried and that iron and manganese oxides are the best overall adsorbents. Prediction of the amount and kind of adsorption with respect to specific solid phases under various conditions does not appear possible, at least with much confidence; but it is apparent that adsorption is important in the concentration of minor elements. All these controlling factors, in addition to diadochy of minor elements in major mineral phases, have apparently been of varying importance in the concentration of minor elements in the rocks of the Meade Peak member.

#### ELEMENT RELATIONSHIPS IN THE VANADIFEROUS ZONE

Beds P-71 through P-75, totaling 3.5 feet, compose an extraordinary rock unit that contains an average of 0.7 percent  $V_2O_5$  and, for a majority of beds in the zone, greater than modal concentrations (pl. 29) of copper, zinc, lead, chromium, and molybdenum—elements included in Krauskopf's (1956) investigations. In addition, the unit is rich in carbonaceous material and contains about 10 percent total sulfur (expressed as  $SO_2$ ) that occurs, in part, as sulfide and probably, in part, as an organic complex.

Although not identified in this section, the occurrence of zinc as sphalerite in the correlative vanadiferous zone of Paris, Idaho (A. D. Weeks, written communication, 1956), is an example of a minor element occurring in a sulfide formation. On the basis of Krauskopf's work Cu and Pb could occur, in part at least, in this manner also. Copper, zinc, and lead, however, are elements that are strongly adsorbed by many kinds of materials, and it seems possible that they might have been concentrated first by adsorption on the carbonaceous material or mineral phases and could have formed sulfides secondarily. Chromium probably occurs as an hydroxide as mentioned previously. Molybdenum enrichment is probably a result of biologic processes, as suggested by Krauskopf (1956, p. 31), although no direct evidence is available here. The unusual concentration of vanadium is difficult to explain. Its mode of occurrence is not known, although, as mentioned previously, its occurrence in a mica or clay mineral has been suggested. Krauskopf (1955, p. 421) cites two principal kinds of occurrence—in micas and in organic compounds. Sulfide formation

should not be a major control of vanadium on the basis of solubility (Krauskopf, 1956, p. 14), and in some black shales sulfur and vanadium are not associated (Krauskopf, 1955, p. 421). In this vanadiferous zone, however, sulfur is abundant and the possibility of some vanadium occurring as a sulfide cannot be excluded. Krauskopf (1956, p. 31) suggests that biological processes may play a large role in concentrating vanadium, an explanation compatible with the rock characteristics but also one that cannot be evaluated with the data at hand. In summary, the concentration of minor elements in the rocks of the vanadiferous zone is not due to any single factor, but rather to a number of factors closely related to the general conditions of an environment in which organic materials play a principal role.

#### SELENIUM

Nine samples from this section, 4 phosphorites and 5 quartz-silicate rocks, have been chemically analyzed for selenium (table 5).

The samples of quartz-silicate rocks show the presence of a concentration of selenium that is about 10 times greater than that found in the phosphorites. Unpublished analyses of samples from other localities show that some phosphorites and oil-rich shales contain selenium in about the same relative amount as that found in the quartz-silicate rocks of this section. Selenium is not, however, consistently associated with the organic component of the rocks, as some of the carbonaceous-rich rock contains only very little selenium. The quartz-silicate rocks of this section that were analyzed for selenium are from the vanadiferous zone, which is rich not only in carbonaceous material but also in sulfur. The association of sulfur and selenium is predictable on the basis of their chemical properties and is found in natural occurrences; Coleman and Delevaux (1957, p. 513) detected selenium in significant amounts (as much as 18 percent) in some sulfides from sedimentary rocks, and A. D. Weeks (written communication, 1956) identified selensulfur in samples of the vanadiferous zone

TABLE 5.—*Chemical analyses of selenium in samples from parts of the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyo.*

[Analysts: J. A. McCarthy, J. L. Siverly, and H. Levine, U.S. Geological Survey]

Bed	Rock type	Percent Se
P-98-----	Phosphorite-----	0.001
97-----	do-----	.001
96-----	do-----	.002
95-----	do-----	.001
75-----	Quartz-silicate-----	.015
74-----	do-----	.015
73-----	do-----	.015
72-----	do-----	.010
71-----	do-----	.009

of the Meade Peak member at Paris, Idaho. However the generally poor correlation of sulfur and selenium for rocks of the Phosphoria obscures the principal factor, or factors, controlling the concentration of selenium; but the controls are probably of the kind investigated by Krauskopf (1956) and discussed previously with respect to the concentration of other minor elements.

#### URANIUM

Chemical and radiometric determinations of uranium have been made on samples from all beds of the section (table 1). The average uranium content of the member is 0.004 percent and ranges from 0.0005 to 0.034 percent. A sample of part of bed P-96 contains 0.060 percent uranium (Thompson, 1953, p. 56), the greatest concentration found in the Phosphoria formation. The chemical analyses in table 1 clearly indicate a general correlation of the percentage of uranium and the percentage of  $P_2O_5$ , but Thompson (1953) has found that the correlation of equivalent uranium and  $P_2O_5$  in phosphorites is consistently good only among samples in which the average percentage of equivalent uranium is high. Thompson has found also that equivalent uranium and organic matter generally are negatively correlated, but one group of samples with a low average content of equivalent uranium did show a positive correlation. This may indicate, as suggested by McKelvey and Carswell (1956, p. 485), that small amounts of uranium occur in some organic matter but that large amounts occur only in the phosphate mineral, carbonate-fluorapatite. Despite complications of this kind, the overall correlation of uranium and  $P_2O_5$  is good, and the work of Altschuler and others (1954, p. 1225) shows that uranium occurs in apatite as a tetravalent ion in substitution for calcium.

No attempt has been made to study the detailed relationships of uranium in this section, but such large-scale studies by others are in progress. Much about the occurrence of uranium in rocks of the Phosphoria, however, is already known, and reference should be made to more complete studies by McKelvey and Nelson (1950), McKelvey, Everhart, and Garrels (1955), and Thompson (1954), in addition to the references mentioned previously.

#### MINERAL COMPOSITION

The suite of minerals found in the Meade Peak member is unusual only with respect to the occurrence of carbonate-fluorapatite (carbonation fluorapatite of Palache, Berman, and Frondel, 1951, p. 884) and fluorite; the other minerals are common constituents of sedimentary rocks. Carbonate-fluorapatite makes up about 28 percent of the member and is the most abundant single mineral, though quartz

and the silicate minerals together compose about 33 percent. Other major constituents in order of abundance are dolomite, 21 percent; calcite, 8 percent; and carbonaceous material, about 5 percent. The silicate minerals are orthoclase, microcline, albite, muscovite, biotite, illite, kaolinite, tourmaline, titanite (sphene), and zircon. Iron oxides are represented by limonite and hematite, and iron sulfides by pyrite and possibly a simple iron sulfide ( $\text{FeS}$ ). Fluorite is a minor constituent of many phosphorites. The character of the mineral suite is essentially constant throughout the member, and the many different rock compositions are due principally to different mineral proportions rather than to different mineral suites.

#### MINERAL-NORM CALCULATIONS

Mineral norms are calculated from the chemical analyses for apatite, dolomite, and calcite; a mineral-group estimate of quartz plus the silicate minerals; and a rough estimate of carbonaceous material. These calculations are shown graphically in the rock-composition column of plate 28, and the values for carbonate-fluorapatite, dolomite, and calcite are listed in table 6.

Carbonate-fluorapatite is the only phosphate mineral present and all phosphorus is assigned to that mineral. Its composition, however, is not precisely known owing to the difficulty, in obtaining pure separates for analysis and owing to its complex composition, as discussed on page 98. Carbonate-fluorapatite is assumed to contain approximately 38 percent  $\text{P}_2\text{O}_5$ ; and a factor of 2.6 times the percentage of  $\text{P}_2\text{O}_5$  in the rocks provides an estimate of their carbonate-fluorapatite content.

Normative dolomite is calculated by multiplying the percentage of  $\text{MgO}$  by the factor 4.58. This assumes that magnesium occurs only in dolomite. It is known, however, that magnesium substitutes for calcium in calcite in small amount, though this is largely counterbalanced by some substitution of calcium for magnesium in the  $\text{MgCO}_3$  phase of dolomite. Some magnesium may occur in carbonate-fluorapatite or illite, but the amount in such occurrences cannot be large and does not reduce the usefulness of the normative calculation of dolomite. Nevertheless, the calculation results in maximum values for dolomite; and that the values do tend to run high is indicated by the comparison of calcite-dolomite ratios (table 7) determined from chemical analyses with those determined from X-ray analyses.

Calcite is calculated by multiplying the  $\text{CO}_2$  not assigned to dolomite and carbonate-fluorapatite by the factor 2.27. The calculation is made from  $\text{CO}_2$  rather than from  $\text{CaO}$  because the assignment of  $\text{CaO}$  is complicated by its occurrence in many other minerals, such

TABLE 6.—*Mineral norms, in percent by weight, for carbonate-fluorapatite, dolomite, and calcite in the Meade Peak phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyo.*

Bed	Carbonate-fluorapatite	Dolomite	Calcite	Bed	Carbonate-fluorapatite	Dolomite	Calcite
P-107-----	2.0	50.8	21.6	P-53-----	54.6	4.6	-----
106-----	66.2	2.2	-----	52-----	21.1	59.5	9.3
105-----	8.4	3.8	-----	51-----	63.3	3.5	-----
104-----	16.0	3.1	-----	50-----	11.5	36.6	24.7
103-----	11.3	2.9	-----	49-----	67.6	4.5	-----
102-----	1.7	19.2	2.7	48-----	10.5	60.5	4.8
101-----	11.7	4.1	2.3	47-----	7.9	63.7	5.2
100-----	67.3	1.8	3.8	46-----	12.6	45.3	6.1
99-----	2.1	45.8	10.7	45-----	75.0	1.8	4.5
98-----	77.5	1.1	5.4	44-----	68.2	2.6	-----
97-----	85.5	0.9	-----	43-----	76.1	2.6	-----
96-----	70.7	1.7	-----	42-----	11.5	58.6	5.4
95-----	77.5	1.6	-----	41-----	28.0	8.7	-----
94-----	69.9	1.6	-----	40-----	4.0	38.5	2.3
93-----	85.0	1.1	-----	39-----	32.0	6.9	-----
92-----	56.2	1.8	-----	38-----	4.9	56.8	3.0
91-----	9.9	17.4	0.7	37-----	12.4	47.2	3.6
90-----	0.5	22.4	32.0	36-----	18.4	41.7	5.2
89-----	76.2	1.5	-----	35-----	60.7	1.9	-----
88-----	62.6	1.9	22.0	34-----	78.0	0.9	-----
87-----	54.7	1.9	-----	33-----	21.1	2.9	-----
86-----	71.4	1.4	-----	32-----	18.7	24.7	2.0
85-----	71.3	1.3	6.1	31-----	47.1	1.8	-----
84-----	42.9	2.0	0.7	30-----	20.8	13.7	0.4
83-----	76.4	1.2	0.7	29-----	15.6	22.0	1.8
82-----	5.5	9.6	36.5	28-----	16.6	43.5	4.1
81-----	10.5	19.2	1.4	27-----	68.4	2.1	-----
80-----	25.7	4.1	16.1	26-----	67.9	6.9	0.7
79-----	5.6	10.1	12.7	25-----	76.7	2.7	-----
78-----	74.5	2.0	-----	24-----	74.4	2.7	1.1
77-----	25.8	7.8	22.2	23-----	69.4	3.7	0.9
76-----	0.9	8.2	82.4	22-----	54.9	10.1	1.1
75-----	7.1	8.7	1.6	21-----	42.6	16.9	2.0
74-----	0.9	10.5	2.0	20-----	33.3	22.9	1.8
73-----	0.5	12.4	-----	19-----	40.3	15.1	1.4
72-----	0.1	13.3	-----	18-----	17.9	41.2	7.9
71-----	16.4	6.4	6.8	17-----	34.6	27.0	5.4
70-----	2.1	8.2	57.6	16-----	13.5	55.9	14.1
69-----	21.6	2.4	-----	15-----	56.0	11.0	1.8
68-----	2.0	11.0	-----	14-----	16.6	56.3	5.9
67-----	15.6	2.2	-----	13-----	40.8	30.7	5.0
66-----	1.7	24.7	25.4	12-----	29.9	46.2	5.9
65-----	25.9	5.5	6.8	11-----	75.1	2.7	2.0
64-----	3.9	39.4	10.0	10-----	19.5	16.9	-----
63-----	32.2	3.7	6.1	9-----	25.2	43.5	1.4
62-----	35.6	4.6	10.0	8-----	53.6	2.6	-----
61-----	1.8	24.3	42.0	7-----	13.0	3.7	-----
60-----	5.8	56.3	7.5	6-----	0.7	26.6	1.4
59-----	37.2	15.6	-----	5-----	0.8	13.7	-----
58-----	5.5	69.2	6.8	4-----	1.1	4.0	-----
57-----	35.4	2.9	-----	3-----	0.4	3.3	-----
56-----	5.8	68.7	8.6	2-----	1.7	6.4	-----
55-----	38.6	27.9	0.4	1-----	75.5	8.7	-----
54-----	14.0	49.9	18.4				

as carbonate-fluorapatite, dolomite, albite, titanite, and fluorite. In using  $\text{CO}_2$  as the base, the calcite calculation is low if dolomite is estimated too high; it also depends upon the amount of  $\text{CO}_2$  assigned to carbonate-fluorapatite. The amount of  $\text{CO}_2$  in carbonate-fluorapatite is taken as 2 percent, a value more likely too low rather than too high.

The acid-insoluble determinations given in table 1 are good estimates of the amount of the quartz-silicate group of minerals present, although the values are consistently low owing to the partial solution of some minerals. It is not possible to approximate even roughly the amount of the principal individual silicate minerals because of the complexity of their assemblage and the lack of precision of the analyses. However, a rough estimate of quartz content can be made by using the silica-aluminum ratios of the principal silicate minerals. The theoretical ratio for orthoclase and albite is about 3.5, and the ratio for muscovite, illite, and kaolinite generally ranges from 1.2 to about 2.0. If an intermediate value between these two groups is taken, the amount of silica combined in silicate minerals can be estimated; the quartz is then estimated by subtracting the combined silica from total silica. For example, if a ratio of 2.5 is used, bed P-3 contains 49 percent quartz, the greatest amount of all the beds, and 22 percent combined silica; and P-45 contains 2 percent quartz, the least amount of all beds, and 3 percent combined silica.

The amount of carbonaceous material in the rocks is calculated as the difference between the loss-on-ignition determination and the sum of the  $\text{CO}_2$  and  $\text{H}_2\text{O}$ —determinations (see table 1). Besides carbonaceous material, these values include structural water from clay minerals, sulfur from iron sulfides, and possibly—as Jacob and others (1933) have found—some fluorine and silica that volatilizes at high temperatures. The calculated amount of carbonaceous material is, therefore, consistently high.

#### COMPARISON OF PERCENTAGE RATIOS OF CALCITE TO DOLOMITE

Chemical and X-ray analyses permit independent calculation of the percentage ratio of calcite to dolomite in carbonate rocks. The amount of calcite and dolomite in 15 end-member rocks has been calculated from the chemical analyses as previously described, and are the values used throughout this study. These values have been checked, however, by a method of X-ray analysis, which is based on the observation that the ratio of X-ray diffraction intensities (peak heights) of calcite to dolomite is a good means of estimating their percentage ratios.

The two sets of estimates of the percentage ratio of calcite to dolomite in the 15 end-member carbonate rocks are given in table 7 along with the calculation of "Student's"  $t$ , a test of the hypothesis that the two sets of paired data are not significantly different. The calculated  $t$  value of 0.55 is far below the  $t$  value of 2.14 at the 5-percent probability level, indicating with considerable confidence that the hypothesis may be valid. However, the data (table 7) show that (a) the variation between individual measurements is relatively large, indicating poor precision in measurement by one or both methods, and that (b) 12 of the 15 ratios determined from X-ray analyses are larger than those determined by the chemical method, indicating a systematic difference between the 2 sets of values that is counterbalanced in the total summation of differences by 2 exceptionally large negative differences in which the ratios calculated from chemical analyses are larger.

TABLE 7.—Comparison of percentage ratio of calcite to dolomite as determined by using two independent methods

$$[\bar{X}=0.043; s^2=0.0899; t=0.55; P_{0.05}=2.14]$$

Sample from bed—	Method of analysis		Difference (1-2)
	X-ray <sup>1</sup> (1)	Chemical <sup>1</sup> (2)	
P-107-----	1. 741	1. 629	0. 112
99-----	1. 386	1. 369	. 017
90-----	2. 337	2. 155	. 182
76-----	3. 277	3. 002	. 275
70-----	3. 120	2. 846	. 274
60-----	1. 142	1. 124	. 018
58-----	1. 014	. 993	. 021
54-----	1. 135	1. 567	— . 432
50-----	1. 046	1. 829	— . 783
48-----	. 865	. 899	— . 034
47-----	. 973	. 912	. 061
46-----	1. 565	1. 129	. 436
42-----	1. 048	. 965	. 083
38-----	. 938	. 723	. 215
37-----	1. 084	. 882	. 202

<sup>1</sup> Percentage ratio of calcite to dolomite is calculated by using the expression

$$\log 100 \frac{\text{percent calcite}}{\text{percent dolomite}}.$$

In summary, the test in which the two sets of values are compared indicates that within the precision of measurement of the ratios, the two methods yield the same results. However, the lack of precision makes the comparison unsatisfactory; and the extremely large variation of a few measurements may have occurred by chance in such a way so as to obscure a significant difference between the two methods of determination.



## MINERALOGY

## CARBONATE MINERALS

Dolomite and calcite are the carbonate minerals of the section and one or both minerals occur in all beds. Dolomite is more abundant than calcite and is found in all parts of the section, although it is concentrated more in the lower half as shown in the columnar section, plate 1. Both dolomite and calcite occur mostly as fine-size particles, commonly mixed with one another in a large range of proportions. Fossil fragments are not common.

Dolomite and calcite are the common carbonate-rock minerals and have been studied intensively; yet much about their natural occurrences is imprecisely or poorly known. An extensive summary of most of the known properties of calcium and magnesium carbonates has been made by Graf and Lamar (1955). The application of X-ray techniques, one of which is previously mentioned (p. 76) in conjunction with other types of analysis, to the study of dolomite and calcite is providing valuable new information on the composition of the minerals and on their proportions in carbonate rocks. These data, though limited at the present time, are contributing to a better understanding of the conditions under which these minerals have formed.

## DIADOCHY IN DOLOMITE AND CALCITE

Diadochy (ionic substitution) for calcium or magnesium in calcite and dolomite is well known for some elements, such as manganese and strontium for calcium, and iron and manganese for magnesium. The kind of diadochy is determined principally by the radius and valence of the ions. Ions larger than calcium, which has a radius of 0.99 Å (Ahrens, 1952, p. 168), such as strontium (1.12 Å) and barium (1.34 Å), substitute for calcium in calcite in small amount because of the size limitation imposed by the calcite structure. They are diadochic in greater amount in the aragonite structure, which tends to be stabilized by them (Faivre, 1944; Faivre and Chaudron, 1948). Manganese (0.80 Å), intermediate in size between calcium (0.99 Å) and magnesium (0.66 Å), is diadochic in all proportions with calcium between the calcite and rhodochrosite end members on the basis of the range of proportions found in samples by Wayland (1942) and Krieger (1930), but the experimental work of Goldsmith and Graf (1957) indicates that the complete range of diadochy is only possible at temperatures greater than 550° C and under a pressure of CO<sub>2</sub> sufficient to prevent decomposition. Diadochy of manganese and magnesium in all proportions between dolomite and mangandolomite appears possible (Winchell, 1951, p. 73). Magnesium (0.66 Å) and iron (0.74 Å) are diadochic in all proportions between dolomite and ankerite (Palache, Berman, and Frondel, 1951, p. 212; Winchell, 1951, p. 73), though compositions

near the ankerite end member are apparently rare. Ferrari and Colla (1936) have found that cobalt (0.72 Å), zinc (0.74 Å), and cadmium (0.97 Å) are diadochic with calcium and magnesium to various degrees, and many other elements probably occur naturally in such relationships. Although substitution for calcium and magnesium in calcite and dolomite is common, substitution for carbon or oxygen in the carbonate radical is not known.

Diadochy of calcium and magnesium for one another in dolomite and calcite is theoretically prohibited because of their large difference in size—0.99 Å for calcium as compared to 0.66 Å for magnesium, a difference much larger than the empirical limit of 15 percent for those ions that readily substitute for one another in nearly all proportions. Magnesium, however, substitutes for calcium in the calcite of the tests of modern organisms in amounts commonly more than 10 percent by weight equivalent  $\text{MgCO}_3$  and as much as 29 percent (Chave, 1952 and 1954a; Goldsmith and others, 1955; and Clarke and Wheeler, 1922). Most calcitic fossils contain less than 10 percent  $\text{MgCO}_3$  (Chave, 1954b, p. 595), as does much natural calcite (Goldsmith and others, 1955, p. 222 and 223) and much recently deposited calcareous sediment (Chave, 1954b, p. 598). Most of the magnesium in calcite formed at low temperatures is unstable (Graf and Goldsmith, 1955, p. 109), but highly magnesian calcites are stable at high temperatures, although the relationships near the dolomite composition end are not known (Harker and Tuttle, 1955; and Graf and Goldsmith, 1955).

Thus although considerable information is available on the diadochy of magnesium for calcium in calcite, virtually nothing is known of the diadochy of these ions for one another in their ordered positions in natural dolomite. Small variations of the calcium-magnesium atomic proportion in high-temperature synthetic dolomite were noted by Harker and Tuttle (1955, p. 278) but were not considered significant. In other high-temperature synthetic dolomite work, Graf and Goldsmith (1955, p. 124) measured as much as 5 mole percent excess  $\text{CaCO}_3$  in dolomite. It should be pointed out in considering diadochy in calcite and dolomite that the two minerals are not strictly isomorphic. Dolomite has an ordered arrangement of calcium and magnesium atoms that occur in alternating planes normal to the trigonal axis. All the magnesium substitution in calcite is of a random or disordered nature, and Harker and Tuttle (1955, p. 74) suggest that a disordered dolomite may be stable at high temperatures. Graf and Goldsmith (1955, p. 124) found 1–1½ mole percent  $\text{CaCO}_3$  in some synthetic high-temperature ordered dolomites. It is clear that more information is needed on these relationships.

A measure of the approximate amount of diadochy in the calcite

and dolomite of 14 end-member carbonate rocks of this section was made by X-ray powder analysis using the Norelco spectrometer and chart recorder. The method consists of the measurement of the amount of shift (degrees  $2\theta$ ) of the most intense peak of calcite and dolomite with respect to standard calcite and dolomite, and the correlation of the shift with the element or elements in diadochy that produced it. The measurements were made with reference to quartz as shown in figure 6.

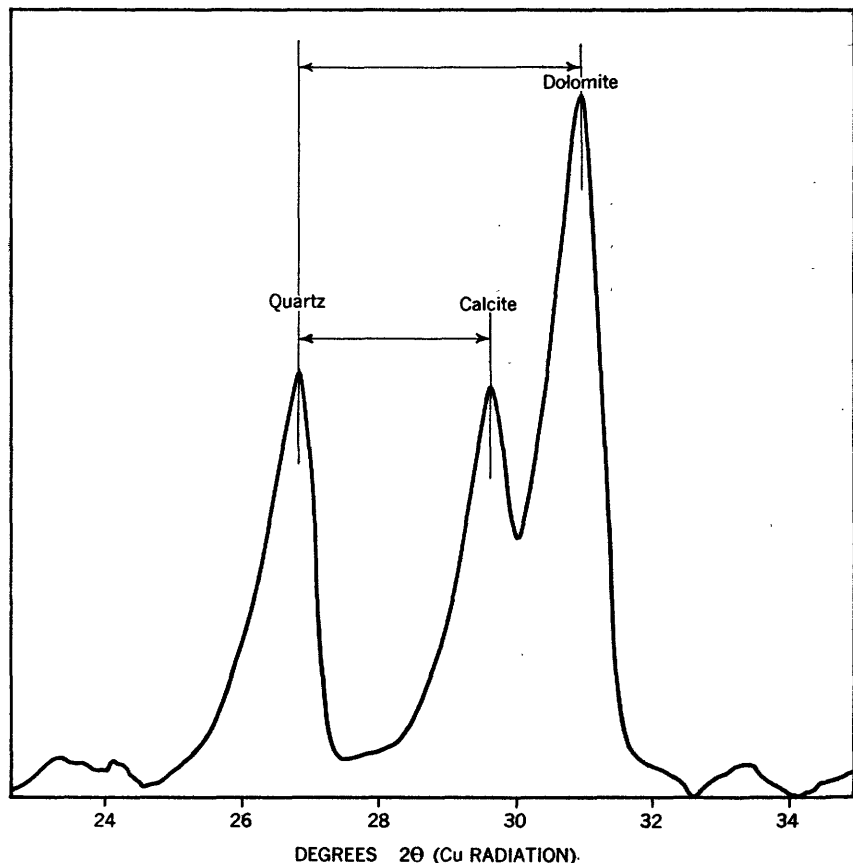


FIGURE 6.—Method of measurement of diadochy in calcite and dolomite, using quartz as reference, by X-ray diffraction analysis.

The dolomite-quartz interval was measured in the 14 samples of carbonate rocks, and the calcite-quartz interval was measured in all but one of the samples. Since the precision of measurement with this equipment was not high, the values were averaged to give mean dolomite-quartz and calcite-quartz intervals. These averages were then compared with average values of the same kind obtained on 14

samples of prepared mineral mixtures that all contained quartz and varying proportions of calcite and dolomite standards (see table 8). The peak shifts for dolomite and calcite determined in this manner are not large (table 9) but can be considered significant on the basis of the *t* test. These mean peak-shift values are considered representative of the amount of diadochy in the dolomite and calcite of this section.

TABLE 8.—*Spectrographic analyses, in percent, of dolomite and calcite standards*

[Calcite from near Manuel Benevides, Chihuahua, Mexico; analyzed by R. Allen for Miller (1952).  
Dolomite locality unknown; analyzed by H. L. Lovell, Pennsylvania State Univ.]

Calcite <sup>1</sup>	Range		Dolomite <sup>2</sup>	Range	
	From—	To—		From—	To—
Al.....	0.001	0.01	Ba.....	0.01	0.1
Ba.....	.001	.01	Co.....	.01	.1
Mg.....	.001	.01	Cu.....	0.01	
Sr.....	.01	.1	Fe.....	.1	1.0
Ti.....	.001	.01	Mn.....	.01	.1
V.....	.001	.01	Na.....	0.01	
			Sr.....	.1	1.0
			Zn.....	.01	.1

<sup>1</sup> As, Ag, B, Bi, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Na, Ni, Pb, Sb, Sn, W, Zn, and Zr were looked for but not detected.

<sup>2</sup> Al and Ni were looked for but not detected.

The amount of diadochy with respect to one element in terms of its equivalent carbonate is determined from the graph (fig. 7) on which the ordinate represents the shift from pure calcite and the abscissa is composition. The linear relation between peak shift and composition is assumed for most of the compositional range between calcite and the end members—magnesite, siderite, and rhodochrosite. The relationship is supported, however, in the high (more than 50 percent) calcite range by the data on magnesium diadochy from Goldsmith and others (1955, p. 215) and Harker and Tuttle (1955, p. 279), and by the fact that dolomite falls very close to the theoretical disordered "dolomite"; and the linear relationship also applies to manganese diadochy in this same range, as shown by Andrews (1950, p. 92), using Krieger's data; but no data of this kind dealing with iron are available, though it is reasonable to expect that the relationship applies equally well to diadochy of iron. In figure 7 the mean value of the peak shift of the calcite in the rock samples from standard calcite ( $d(104)=3.037$  Å) is plotted on the calcite-magnesite join, and represents an amount of diadochy in terms of magnesium of about 0.4 percent or as equivalent  $\text{MgCO}_3$  of about 1.5 percent. A slightly greater amount of either iron or manganese could produce the same shift in the calcite peak. Spectrographic analyses of these samples show insufficient manganese

to account for the shift. Elements with ionic radii larger than calcium, such as strontium and barium, would cause a peak shift in the opposite direction to the one observed, and they are excluded on that basis as well as for the fact that they occur in very small amounts in these

TABLE 9.—Comparison of the mean difference between the most intense X-ray peaks of calcite and dolomite and quartz in carbonate rocks and in prepared mineral mixtures

Calcite-quartz interval:  $\bar{X}_1 - \bar{X}_2 = 0.0499$ ; pooled  $s^2 = 0.003464$ ;  $t = 2.20$   
and is significant at  $P_{0.05}$  probability level.

Dolomite-quartz interval:  $\bar{X}_1 - \bar{X}_2 = 0.0757$ ; pooled  $s^2 = 0.003492$ ;  $t = 3.39$   
and is significant at  $P_{0.01}$  probability level.

Carbonate rocks		Prepared mineral mixtures	
Sample from bed—	Degrees 2 $\theta$ (copper radiation)	Sample	Degrees 2 $\theta$ (copper radiation)
<b>Calcite-quartz interval</b>			
P-37	2. 82	1	2. 79
42	2. 83	2	2. 68
46	2. 82	3	2. 75
47	2. 80	4	2. 70
48	2. 95	5	2. 82
50	2. 78	6	2. 73
54	2. 70	7	2. 74
58	2. 87	8	2. 77
70	2. 70	9	2. 78
76	2. 81	10	2. 69
90	2. 80	11	2. 67
99	2. 78	12	2. 77
107	2. 72	13	2. 80
		15	2. 79
$\bar{X}_1$	2. 7985	$\bar{X}_2$	2. 7486
$SS_1$	. 0564	$SS_2$	. 0302
<b>Dolomite-quartz interval</b>			
P-37	4. 25	1	4. 36
38	4. 26	2	4. 28
42	4. 20	3	4. 34
46	4. 18	4	4. 39
47	4. 28	5	4. 29
48	4. 40	6	4. 26
50	4. 26	7	4. 35
54	4. 22	8	4. 34
58	4. 24	9	4. 35
70	4. 21	10	4. 21
76	4. 32	11	4. 28
90	4. 26	12	4. 33
99	4. 17	13	4. 30
107	4. 12	15	4. 35
$\bar{X}_1$	4. 2407	$\bar{X}_2$	4. 3164
$SS_1$	. 0607	$SS_2$	. 0301

samples. Hence magnesium and iron are the likely substitutions that have caused the peak shift, but there is no sound basis for determining the contribution of either; and the total amount in diadochy is so small that their determination is not significant.

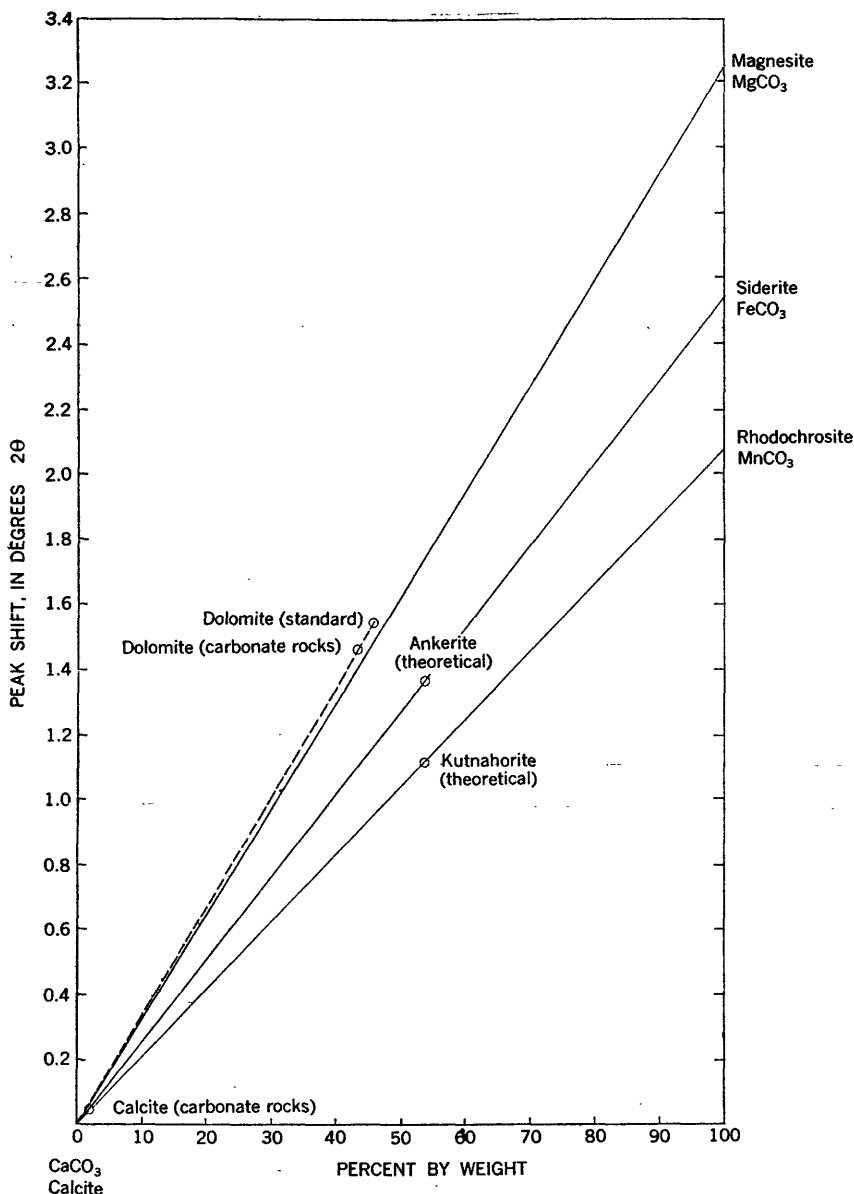


FIGURE 7.—Graph showing relation of X-ray peak to composition between some end-member carbonate minerals and to composition of dolomite and calcite in carbonate rock samples

The mean peak shift of the dolomite in the rock samples from standard dolomite ( $d=2.887$ ) is plotted in figure 7 on the calcite-dolomite join, which is slightly offset from the calcite-magnesite join. This peak shift is toward calcite and indicates substitution of an ion with a radius greater than that of magnesium in the magnesium positions or one greater than that of calcium in the calcium positions. The latter type of diadochy is unlikely to occur for the same reasons discussed above with respect to calcite. Manganese and iron are common ions that are larger than magnesium and theoretically could produce the shift; however, using the theoretical positions of kutnahorite and ankerite in figure 7 and assuming a linear relationship, the observed peak shift of the dolomite in the rock samples would require about 10 percent  $\text{MnCO}_3$  or 24 percent  $\text{FeCO}_3$  in substitution for magnesium—neither of which is possible. Kutnahorite has an ordered dolomite structure (Fron del and Bauer, 1955, p. 749), and presumably ankerite does too; thus the theoretical positions plotted in figure 7 are only approximations, which are close enough for the purpose here. Calcium, however, is larger than magnesium and very likely substitutes for magnesium in an amount of about 1 percent calcium or 2.5 percent equivalent  $\text{CaCO}_3$ .

The small amount of diadochy found in the dolomite and calcite of the carbonate samples studied very likely represents a stable relationship, which conforms, with respect to calcium-magnesium diadochy at least, to general low-temperature extrapolations from the high-temperature relations determined by Graf and Goldsmith (1955, p. 125) and Harker and Tuttle (1955, p. 279). Approximately 1.5 percent  $\text{MgCO}_3$  occurs in the calcite of these samples if all the diadochy is attributed to magnesium. The amount of  $\text{MgCO}_3$  is similar to that of the general mode found in pre-Cenozoic calcitic fossils and to that of one mode in Paleozoic limestone (Chave, 1954b, p. 595 and 598), and it is markedly less than the amount most commonly found in the calcite of Cenozoic fossils and modern skeletons. These data are inadequate at present for determining the various conditions under which natural calcite has formed, but more such work on calcite, as well as on dolomite for which there is now few compositional data, offers promise of aiding the achievement of this goal. The various amounts of magnesium held metastably in the calcitic skeletons of modern marine organisms have an important bearing on the significance of the dolomite-calcite proportions found in the older rocks, if it is presumed that similar amounts of magnesium occurred in fossils, which formed, with time, equivalent amounts of dolomite virtually in place. In addition to the calcium and magnesium relationships, quantitative determination of minor ele-

ments—particularly strontium, manganese, and iron—in calcite and dolomite should be helpful. Strontium may be a valuable indicator on the basis of work done by Zeller and Wray (1956); Turekian and Kulp (1956); Kulp, Turekian, and Boyd (1952); Murray (1954); and Lowenstam (1954). The semiquantitative determinations on the carbonate rocks of this section all indicate less than 0.1 percent and most less than 0.01 percent strontium, which suggests that these rocks average a smaller strontium content than does the average limestone with 610 ppm of strontium (Turekian and Kulp, 1956, p. 245).

#### CARBONATE-FLUORAPATITE

The precise chemical composition of the phosphate mineral in the Phosphoria formation has been obscure because of the difficulty of obtaining pure homogeneous samples for analysis and because its composition is complex. Mansfield (1927, p. 367) suggested, but could not satisfactorily prove, that carbonate ( $\text{CO}_3$ ) and fluorine were chemically combined with the calcium phosphate. Subsequent analytical work by Jacob and others (1933) and Hendricks and others (1931) noted the relationship of carbonate with the mineral and conclusively established that the mineral is a fluorine apatite. However, the occurrence of carbonate as a structural component of the phosphate mineral of the Phosphoria formation has been in doubt and has been part of a controversy involving the validity of carbonate apatites in general. The problem has been to determine whether the carbonate occurs as calcium carbonate intimately mixed with the apatite, as carbonate on occluded surfaces (Hendricks and Hill, 1950), or as carbonate occupying lattice positions of the apatite structure. Silverman, Fuyat, and Weiser (1952), in an excellent study of the problem, show by several tests that although calcite is commonly intermixed with apatite, some of the carbonate (approximately 1 to 2 percent equivalent  $\text{CO}_2$ ) occurs homogeneously in the apatite mineral and not on occluded surfaces. X-ray analyses by Altschuler, Cisney, and Barlow (1952) show that carbonate-fluorapatite is a homogeneous phase distinguishable from fluorapatite and hydroxyapatite. Apatite from the Phosphoria formation was tested both by Silverman, Fuyat, and Weiser (1952) and by Altschuler, Cisney, and Barlow (1952); and it is a carbonate-fluorapatite, as are other marine apatites in the United States and in other parts of the world (Altschuler and others, 1952). Although carbonate-fluorapatite is chemically and structurally distinct from other apatites, a dilemma persists about the specific mode of occurrence of the carbonate in the structure. Trautz (1955) has made a general review and detailed study of the problem of the carbonate apatites, but no ex-



planation is entirely consistent with accepted structural principles; furthermore, present terminology is inadequate for describing some of the possible relationships. This aspect of the carbonate-fluorapatite problem is only briefly described in the following section, but detailed studies of the apatite in the Phosphoria formation are in progress.

#### RELATION TO THE APATITE MINERAL GROUP

Carbonate-fluorapatite belongs to the apatite group of minerals having a general formula  $A_5(XO_4)_3Z_q$ . The structure of the group was first described independently by Náray-Szabó (1930) and by Mehmel (1930, 1931). They have both shown that the unit cell of fluorapatite contains 10 calcium, 6 phosphorus, 24 oxygen, and 2 fluorine ions, as indicated in the formula  $Ca_{10}(PO_4)_6F_2$ . In this structure many substitutions have been described, as shown in table 10 (McConnell, 1938). McConnell (1953) has added vanadium, chromium, and possibly aluminum to the list of what he considers to be adequately demonstrated substitutions for phosphorus.

TABLE 10.—*Diadochy in some minerals of the apatite group*<sup>1</sup>

Mineral	Formula
Fluorapatite.....	$Ca_{10}/(PO_4)_6/F_2$
Hydroxyapatite.....	$Ca_{10}/(PO_4)_6/(OH)_2$
Dahlite.....	$(Ca,C)_{10}/(PO_4)_6/(OH)_2$
Dehrnite.....	$(Ca,Na,C)_{10}/(PO_4)_6/(OH)_2$
Francolite.....	$(Ca,C)_{10}/(P,C)_6(O,OH,F)_{24}/F_2$
Lewistonite.....	$(Ca,K,Na,C)_{10}/(PO_4)_6/(OH)_2$
Wilkeite and ellestadite.....	$(Ca,C)_{10}/(P,S,Si,C)_6O_{24}/(Cl,F,OH,O)_2$
Fermorite.....	$(Ca,Sr)_{10}/(P,As)_6O_{24}/(F,OH,O)_2$
Manganapatite.....	$(Ca,Mn)_{10}/(PO_4)_6/F_2$

<sup>1</sup> From McConnell (1938).

Considering all the possible substitutions together, the following general formula is obtained for this group of apatite minerals:



Other minerals of the apatite group belonging to the pyromorphite and svabite series (Palache, Berman, and Frondel, 1951, p. 877) are chemically distinct from the ones considered above because they represent end members for which only few naturally occurring intermediate members with the apatite series are known, particularly with regard to the diadochy of calcium and lead.

The elements in table 11, which have been reported as substitutions in the apatite structure in table 10, show an unusual range in ionic size and charge. Carbon is so extremely small as compared to

TABLE 11.—*Ionic radii (sixfold coordination) and radius ratios of ions in apatite*

Ion	Ionic radius <sup>1</sup> (Å)	Ratio (cation/oxygen)	Ion	Ionic radius <sup>1</sup> (Å)	Ratio (cation/oxygen)
Ca <sup>+2</sup> -----	0. 99	0. 71	Si <sup>+4</sup> -----	0. 42	0. 30
Sr <sup>+2</sup> -----	1. 12	. 80	As <sup>+5</sup> -----	. 46	. 33
Mn <sup>+2</sup> -----	. 80	. 57	V <sup>+5</sup> -----	. 59	. 42
Na <sup>+1</sup> -----	. 97	. 69	Cr <sup>+6</sup> -----	. 52	. 37
K <sup>+1</sup> -----	1. 33	. 95	Al <sup>+3</sup> -----	. 51	. 36
C <sup>+4</sup> -----	. 16	. 11	C <sup>+4</sup> -----	. 16	. 11
U <sup>+4</sup> -----	. 97	. 69			
R.E. <sup>+3,2</sup> -----	. 85-1. 14	. 61-0. 81	O <sup>-2</sup> -----	1. 40	-----
			F <sup>-1</sup> -----	1. 33	-----
P <sup>+5</sup> -----	. 35	. 25	Cl <sup>-1</sup> -----	1. 81	-----
S <sup>+6</sup> -----	. 30	. 21	OH <sup>-1</sup> -----	( <sup>3</sup> )	-----

<sup>1</sup> From Ahrens, 1952.<sup>2</sup> Rare earths, including lanthanum and yttrium.<sup>3</sup> Similar to O<sup>-2</sup>.

phosphorus and calcium that, from crystal chemical considerations, it would not be expected to substitute for either. In fact, it is this consideration that precipitated the controversy about the mode of occurrence of carbon in apatite minerals. From the study of minerals in which oxygen is the dominant anion, it has been found that the ionic-radius ratio of the cation to oxygen is a principal factor in determining the coordination of oxygen ions about a cation. Table 12 shows the range of radius ratios for the different oxygen coordinations. Ions whose ratios with oxygen fall near the border between two groups have been found to occur in minerals with a coordination of either group. On this basis, carbon generally would be expected to have a coordination of two or three as it commonly does. McConnell (1938) proposed a structurally possible mechanism for the substitution of carbon for calcium, one in which carbon would be coordinated by three oxygen ions, but this proposed mechanism does serious violence to crystal chemical principles. Carbon and phosphorus, in their respective CO<sub>3</sub> and PO<sub>4</sub> groups, each require more than one half the charge of each of their coordinating oxygen ions. Thus their groups cannot share oxygen ions as is required in McConnell's hypothesis.

TABLE 12.—*Coordination of cations <sup>1</sup>*

Oxygen coordination about cation	Position of oxygen ions	Radius ratio (cation/oxygen)
8-----	Corners of a cube-----	1-0. 732
6-----	Corners of a regular octahedron-----	. 732- . 414
4-----	Corners of a square-----	. 732- . 414
4-----	Corners of a regular tetrahedron-----	. 414- . 225
3-----	Corners of an equilateral triangle-----	. 225- . 155
2-----	Linear-----	. 115-0

<sup>1</sup> From Evans, 1948, p. 176.

In the phosphorus position carbon would be coordinated by four oxygen ions and would be located in the center of a tetrahedron, a position at variance with the concepts mentioned above; however, Hendricks and Hill (1942) and McConnell (1952) have proposed that four  $\text{CO}_3$  groups substituting for three  $\text{PO}_4$  groups is possible and would give carbon the desired three-fold oxygen coordination.

However, McConnell's proposed arrangement of the carbonate groups, in which most of the planar  $\text{CO}_3$  groups are oriented parallel to the  $c$  axis, would result in a positive rather than the negative birefringence of apatite. Supporting this arrangement is the fact that the carbonate-containing apatites have a shorter  $a$  axis than do the corresponding carbonate-free ones. The infrared data of Romo (1954), as well as those of Posner and Duyckaerts (1954) and of Underwood and others (1955), are important because they provide concrete evidence of the occurrence of  $\text{CO}_2$  in apatite as  $\text{CO}_3$  groups—always a tacit assumption except for Gruner and McConnell's (1937, p. 213) hypothesis (which McConnell later rejects) that carbon substitutes for phosphorus directly and is coordinated by four oxygen ions.

Explanation of the occurrence of carbonate in the apatite lattice in terms of classical substitution is not entirely satisfactory, but of all the possibilities the substitution of  $\text{CO}_3$  for  $\text{PO}_4$  groups seems most likely. Although other explanations of the gap between true substitution and true inclusion are given by Trautz (1955), knowledge is as yet insufficient to adequately describe and test the possible phenomena.

On the basis of size,  $\text{K}^{+1}$  and  $\text{Cl}^{-1}$  also appear to be unlikely substitutions for  $\text{Ca}^{+2}$  and  $\text{F}^{-1}$ , respectively; however, they seem to occur in some of the apatite minerals in appreciable amounts. Ions of the same valence but of slightly different size generally require in substitution an increase or decrease in the volume of the unit cell, but they do not present the complications resulting from the substitution of ions of different valence. Ions of different valence require compensating substitutions to preserve the overall electrostatic equilibrium of the structure, such as  $\text{S}^{+6}$  and  $\text{Si}^{+4}$  for  $\text{P}^{+5}$ , or  $\text{S}^{+6}$  for  $\text{P}^{+5}$  and  $\text{Na}^{+1}$  for  $\text{Ca}^{+2}$ . Compensating substitutions of this kind are apparently common in apatite minerals but are little understood.

#### DIADOCHY IN THE CARBONATE-FLUORAPATITE OF THE MEADE PEAK MEMBER

Diadochy in the carbonate-fluorapatite of the Meade Peak member has been established previously only for uranium, although the substitution of sodium for calcium has been suggested by Hendricks and others (1931). Other substitutions in significant but small amount, however, are indicated by an appraisal of the analyses of phosphorite in table 13.

A comparison of chemical analyses of the three end-member rock types (table 13) shows that phosphorite contains concentrations of sulfur, sodium, and vanadium, relative to one or both of the other rock types. The mean percentages of the constituents of carbonate and quartz-silicate rocks are compared in turn with the respective mean percentages of phosphorite by a modified *t* test (table 14; Bennett and Franklin, 1954, p. 177) that provides a more precise test than does the "student" *t* of the difference between the means where the variances of the groups are not assumed to be equal.

The amount of sodium in the phosphorite (table 13) is significantly greater than it is in the other rock types, although the apparent excess is only about 0.2 percent  $\text{Na}_2\text{O}$ . Some of the sodium, then, is believed to substitute for calcium in the apatite structure—a relationship that appears to be general for phosphorite of the Phosphoria, as shown by other unpublished analyses.

TABLE 13.—Comparison of the percentages of  $\text{Na}_2\text{O}$ ,  $\text{SO}_3$ , and  $\text{V}_2\text{O}_5$  in phosphorite with that in carbonate and quartz-silicate rocks

Phosphorite	Carbonate rock	Quartz-silicate rock	Phosphorite	Carbonate rock	Quartz-silicate rock
<b><math>\text{Na}_2\text{O}</math></b>			<b><math>\text{SO}_3</math>—Continued</b>		
1.0	0.6	0.3	2.2	0.6	0.9
1.2	.8	.4	3.5	1.7	.3
1.1	.5	.4	2.7	.7	8.4
.8	.8	.2	3.5	.5	1.6
1.0	.5	.2	2.8	.8	3.1
.7	.7	.4	2.9	1.6	8.6
1.0	.7	1.5	2.3	1.0	1.1
1.0	1.3	1.0			
1.0	1.1	.6	$\bar{X}$ .... 2.92	1.00	2.33
1.1	.8	.8			
1.0	.4	1.3	<b><math>\text{V}_2\text{O}_5</math></b>		
.9	1.0	1.2	0.10	0.06	0.11
.9	.9	.6	.15	.07	.08
1.2	.9	1.2	.09	.04	.07
1.2	.8	1.0	.07	.09	.19
$\bar{X}$ ... 1.00	.78	.74	.26	.04	.04
<b><math>\text{SO}_3</math></b>			.08	.07	.04
2.9	0.4	1.6	.10	.05	.08
3.5	1.0	1.1	.13	.05	.04
3.4	.5	.6	.10	.06	.06
2.3	1.6	3.7	.11	.06	.02
3.2	1.1	1.5	.08	.04	.37
2.4	1.7	.8	.11	.06	.06
3.2	1.0	.9	.09	.08	.09
3.0	.8	.8	.06	.08	.36
			.06	.05	.52
			$\bar{X}$ .... .106	.060	.142

TABLE 14.—*Comparison of mean percentages of Na<sub>2</sub>O, SO<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub> in carbonate and quartz-silicate rocks with that in phosphorite, as determined by modified *t* tests*[*t'*: Modified *t* test (Bennett and Franklin, 1954, p. 177)]

Rock type	Na <sub>2</sub> O	SO <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>
Phosphorite and carbonate ( <i>t'</i> )-----	3. 02	11. 44	3. 46
Degrees of freedom-----	<sup>1</sup> 22. 8	<sup>1</sup> 28. 0	<sup>1</sup> 16. 8
Phosphorite and quartz-silicate ( <i>t'</i> )----	2. 21	. 84	. 88
Degrees of freedom-----	<sup>2</sup> 17. 1	14. 8	16. 9

<sup>1</sup> Significant at the 0.01 probability level.<sup>2</sup> Significant at the 0.05 probability level.

Sulfur is concentrated in phosphorite relative to carbonate rock (table 13), but not to quartz-silicate rock. The mode of occurrence of sulfur in phosphorite and quartz-silicate rock is probably different. Jacob and others (1933, p. 49) found that most of the sulfur in Phosphoria phosphorite samples occurs as soluble sulfate, whereas sulfur in the quartz-silicate occurs as sulfide and possibly in some other form. Soluble sulfate in phosphorite is considered to indicate diadochy of sulfur with phosphorus in the apatite; neither gypsum nor anhydrite, the only other likely soluble sulfate compounds, have been found.

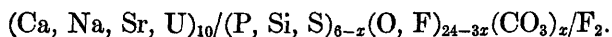
Phosphorite contains more vanadium than does carbonate rock (table 13) but less than quartz-silicate rock. Vanadium may be diadochic with phosphorus here, a substitution in apatite that McConnell (1953) considers substantiated; if so, its mode of occurrence is different than that in quartz-silicate rock.

Wilkeite and ellestadite are minerals in the apatite group that show the diadochic substitution of silicon for phosphorus, and this kind of substitution is also believed to occur in carbonate-fluorapatite. Silicon occurs as acid-soluble silica in phosphorite, as indicated by the fact that the total amount of silica in end-member phosphorite is greater than that of the acid-insoluble material in the rock by an average of 1.7 percent. In contrast, the carbonate and quartz-silicate rocks contain 3.4 and 11.8 percent, respectively, more acid-insoluble material than silica—the common relationship because of the presence of elements other than silicon in insoluble silicate minerals. The amount of soluble silica in phosphorite determined in this manner is not precise, but the estimate of 1.7 percent is probably a minimum.

Spectrographic analyses (table 4) show that silver, zinc, and strontium are also relatively concentrated in end-member phosphorites. The disposition of silver and zinc in the phosphorite is not known, but strontium likely occurs in the apatite structure diadochic with calcium—a common relationship for all phosphorites of the Phosphoria.

Why strontium favors apatite instead of calcite, however, is not known.

Of all the elements described as possibly occurring to some extent in the apatite structure of the phosphate mineral in the Meade Peak member, the substitution of silicon and sodium appears to be best substantiated and significant in amount. Assuming that  $\text{Na}^{+1}$  and  $\text{Si}^{+4}$  are diadochic with  $\text{Ca}^{+2}$  and  $\text{P}^{+5}$ , respectively, other substitutions with cations of higher valence than those of phosphorus and calcium or with anions of lower valence than that of oxygen are necessary to preserve the electrostatic equilibrium of the apatite structure. Thus sulfur ( $\text{S}^{+6}$ ) diadochic with phosphorus tends to satisfy this demand, as does fluorine ( $\text{F}^{-1}$ ) in substitution for oxygen. Fluorine found in the phosphate rocks in excess over that required for the theoretical composition of fluorapatite may well be explained in this manner; that is, fluorine diadochic with oxygen is present in amount necessary to balance, at least partly, the substitution with ions of lower valence, such as sodium and silicon, for calcium and phosphorus. A general formula for the elements most probably occurring as substitutions in the apatite structure is:



It should be emphasized that the kinds of substitutions indicated here by indirect methods need to be verified by direct quantitative analysis.

#### PHOSPHATE MINERAL NAME

Collophane and francolite are names that have been applied, respectively, to isotropic and anisotropic phosphate minerals of the Phosphoria formation, though chemical differences, if any, have not been detected. However, as McConnell (1950, p. 18) and Palache, Berman, and Frondel (1951, p. 885) suggest that collophane be used to designate any cryptocrystalline phosphatic material for which specific mineralogic information is not known, the use of collophane for the phosphate mineral of the Phosphoria formation is no longer desirable.

McConnell (1938, p. 9) suggests that francolite is a suitable name for an apatite which contains an appreciable amount of carbon dioxide and more than 1 percent fluorine. The carbonate-fluorapatite of the Meade Peak member falls well within the definition; however, the name francolite is not inclusive enough for a mineral in the apatite group, which is noted for the number and amount of ionic substitutions in its minerals. Assuming that the diadochy for the apatite described above occurs, the phosphate mineral of the phosphatic shale member would be intermediate between francolite, dehrnite, and wilkeite and ellestadite in composition, as shown in table 10. Because no

adequate name is available, the phosphate mineral in the Meade Peak member is here called descriptively carbonate-fluorapatite, or simply apatite where it is the only phosphate mineral of reference.

#### **SUBMICROCRYSTALLINE CHARACTER OF CARBONATE FLUORAPATITE**

Carbonate-fluorapatite occurs in the Meade Peak member principally as submicrocrystalline isotropic masses. An X-ray analysis shows that it is well developed crystalline material and indicates that its isotropic character is due to the random orientation of submicroscopic particles. Vol'fkovich and others (1952), in an electron-microscope study of natural phosphates, found that the smallest particles are several hundred angstroms in diameter. A possible explanation for this form of development can be derived from the inherent character of the mineral. Crystal growth is a phenomenon depending upon surface forces and their distribution. It seems possible that the asymmetry of forces developed on a crystal surface because of ionic substitutions, such as those of different size and charge previously described, is sufficient to restrict crystal growth to relatively small size; that is, to particles containing relatively few unit cells. It might easily be due to the effect of strong and small ions of high polarizing power on anions that are easily polarized. Thus the forces on a crystal surface would be quite different from those in its interior. Carbon, silicon, phosphorus, and sulfur, in particular, would cause pronounced asymmetry at the surface, polarizing the anions (oxygen and fluorine) to such an extent that the anions would make the principal but weak contribution to the surface energy. A similar phenomenon is described by Weyl (1951, p. 14) about which he says "the equilibrium surface may deviate sufficiently from the ideal surface to make further crystal growth improbable." Trautz (1955, p. 708) visualizes a coprecipitate concentrated along certain layers of the host serving to break the coherence of the structure and limiting crystal size.

#### **FELDSPAR**

Much progress has been made in the past several years toward an understanding of the origin of feldspar. This is due largely to the fundamental work of Bowen and Tuttle (1950) on artificial alkali feldspar and of Tuttle and Bowen (1950) on high albite and high modifications of other kinds of sodic plagioclase. X-ray techniques that they developed for determining composition and high and low modifications have served to simplify and spur on the study of natural feldspar. An additional X-ray technique, described by Smith and MacKenzie (1955), provides a means for obtaining precise information about the phases composing the single-alkali feldspar group. X-ray data, obtained by these X-ray procedures, together with chemical and

optical data on many kinds of feldspar of somewhat well-defined origin (Tuttle, 1952a and 1952b; Tuttle and Keith, 1954; MacKenzie and Smith, 1955 and 1956; and Baskin, 1956) now permit precise identification of feldspar types; and, as these data accumulate, the environment of origin becomes more precisely defined. Although there is still much more to be learned about feldspar, it is now possible to gain some information about the origin of sedimentary rocks that contain feldspars by the identification of the specific type or types of feldspar.

Nearly half the samples of this section were studied by using the X-ray powder method and nearly all were studied in thin section. The small grain size of the material, nearly all silt size except for the apatite pellets, greatly restricts optical work and makes mineral separation prohibitively difficult. Nevertheless, this study of feldspars, particularly the X-ray analyses of acid insoluble material of the samples, has yielded some interesting and useful information even though not entirely complete nor conclusive.

Feldspars were identified mainly from the X-ray powder analyses of acid insoluble material that consists, in addition to the feldspar, mostly of quartz and some illite-muscovite. The presence of quartz and illite-muscovite is undesirable, but fortunately in this particular mineral mixture the coincidence of some X-ray peaks did not prevent the identification of the feldspar. More difficulty is encountered in rocks which contain two kinds of feldspar, as in most of the samples from the section; but even in such rocks, reasonable identification is possible.

Two kinds of feldspar and two modes of occurrence are indicated for the rocks in the section. In one mode of occurrence, orthoclase was the only feldspar present; in the other, orthoclase and albite occurred together. Microcline has been identified in the thin sections of many samples but is minor in amount and was not detected by X-ray methods. In figure 8, X-ray patterns of samples from beds P-6 and P-28 are examples of the orthoclase and orthoclase-albite occurrences. The orthoclase in the sample from bed P-6 is close to its end-member composition as indicated by the fact that its  $\bar{2}01$  peak is located at or very close to  $21^\circ$  (angle of  $2\theta$  using copper radiation), even though the strong quartz peak at that position obscures the weaker orthoclase peak. The  $\bar{2}01$  peak occurs at approximately  $21^\circ$  for pure orthoclase and at about  $22^\circ$  for pure albite. Bowen and Tuttle (1950, p. 491) used the position of this peak for determining the composition of high-temperature alkali feldspar for which there is complete solid solution between the soda and potash end-members. For comparison with the orthoclase in the sample P-6, patterns of sanidine and orthoclase (both perthites that were homogenized by



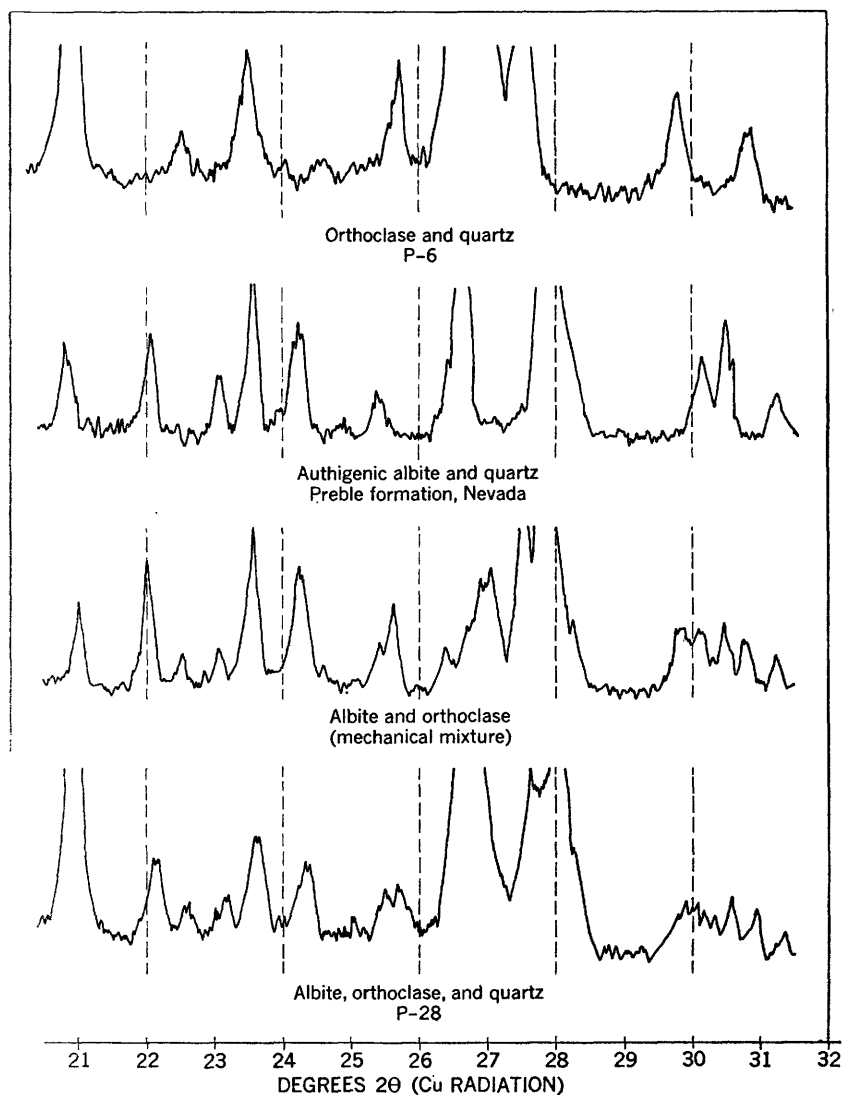


FIGURE 8.—Graph showing partial X-ray patterns of albite and orthoclase and mixtures of the two. A quartz peak near  $21^\circ$  obscures an orthoclase peak. A strong quartz peak obscures orthoclase and albite peaks between about  $26.5^\circ$  and  $27^\circ$ .

heating at  $950^\circ\text{C}$  for 2–3 hours) with compositions of about  $\text{Or}_{50}$  and  $\text{Or}_{75}$  are shown in figure 9.

Orthoclase, where it is virtually the only feldspar present, is believed to be authigenic because of its near end-member composition, nonperthitic character, and petrographic relationships. Baskin (1956), in a comprehensive study of authigenic feldspar, found that it is uniquely pure in composition and that the potassium feldspar rarely

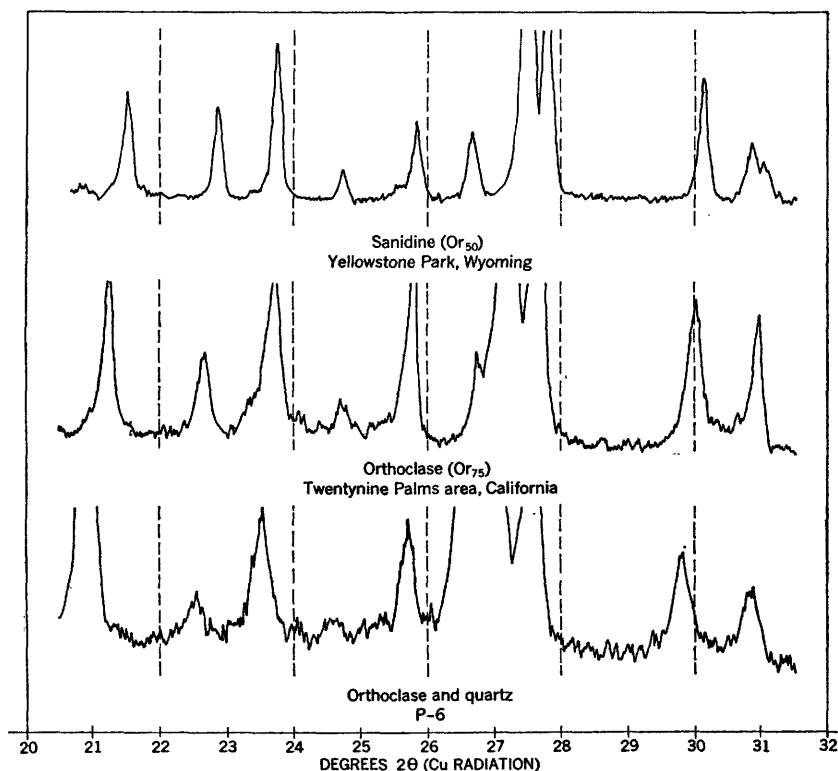


FIGURE 9.—Graph showing partial X-ray patterns of orthoclase and sanidine. Strong quartz peaks (sample from bed P-6) near  $21^\circ$  and also between about  $26.5^\circ$  and  $27^\circ$  obscure orthoclase peaks. Orthoclase ( $Or_{75}$ ) and sanidine ( $Or_{50}$ ) are perthites homogenized by heat treatment.

contains more than 2 percent equivalent albite. In contrast, the potassium feldspar of plutonic salic rocks commonly contains as much as 20–35 percent equivalent albite, including calcium feldspar (Tuttle, 1952b, p. 111), and also is commonly perthitic. An anomalous feature of authigenic potassium feldspar is that it apparently occurs more commonly as the high-temperature monoclinic form than as the low-temperature triclinic microcline. Baskin (1956, p. 151) believes that authigenic monoclinic potassium feldspar forms metastably. Evidence of authigenic development is suggested in thin section by the occurrence of orthoclase in irregularly shaped patches of cement or matrix and by inclusions of carbonaceous material that must have been enveloped by the orthoclase in its growth. Many grains, however, do not show any definitive features of origin; they range in shape from anhedral to subhedral and contain from few to many inclusions of bubbles, illite, and carbonaceous and iron oxide material.

The samples in which orthoclase and albite occur together are more difficult to interpret. In figure 8, the partial X-ray pattern of a

mechanical mixture of orthoclase and albite is presented for comparison with that of a sample from bed P-28. The similarities of the two patterns are apparent, disregarding the two strong quartz peaks of the sample from bed P-28 at approximately  $21^{\circ}$  and  $26.5^{\circ}$ ; yet this comparison is not sufficient in itself for identification, and a detailed study of the position of peaks that might represent other possible kinds of feldspar must be made. Without doubt the feldspar present, other than orthoclase, is plagioclase, but its identification as albite is not as certain. The choice is limited to albite and oligoclase, however, and albite is favored by the X-ray and optical data. The unresolved or poorly resolved X-ray peak at about  $28.3^{\circ}$  is characteristic of albite. This peak shifts to higher angles and is clearly resolved in plagioclase that is more calcic than albite, and it is one of a pair of peaks used by Goodyear and Duffin (1954, p. 319) for determining anorthite content of plagioclase. Indices of refraction and extinction angles favor albite, though neither of these was determined precisely enough for positive identification.

The occurrence of orthoclase and albite together is similar to that of orthoclase alone, and the orthoclase in both occurrences is believed authigenic. The similarities in the occurrence of albite and orthoclase suggest that the albite is probably authigenic, too. If the feldspar in these rocks is mostly authigenic, the problem of their different occurrences must still be explained. Orthoclase is the only feldspar in the rocks composing about the lower one-quarter of the section in which it comprises as much as 15-20 percent of some of the quartz-silicate rocks—the most of any rocks in the entire section. In the upper three-quarters of the section, most of the rocks contain orthoclase and albite, although orthoclase frequently occurs alone. There is no apparent correlation between the mode of occurrence of feldspar and that of the major rock types. The amount of feldspar in a rock, however, is roughly proportional to the amount of quartz. Thus the constituents from which the feldspar formed were apparently derived ultimately from the same source as the quartz. Volcanic glass is a possible source material for the feldspars and is often cited as a possibility (for example, Honess and Jeffries, 1940, p. 17), but this is not well substantiated. The rare occurrence of biotite in a few samples and the characteristics of some of the quartz (see p. 110) suggest a volcanic origin for some of the material, but this evidence is not conclusive.

Although an authigenic origin for the feldspar in the rocks of the section is favored, the orthoclase-albite association might actually be an orthoclase cryptoperthite, that is, a perthite of orthoclase and albite phases, as detected by X-ray methods, that appears to be a

homogeneous feldspar under the microscope. This alternative is not readily excluded by petrographic data since twinning is not common, and where twinning is present it is commonly fuzzy. Since perthites can be homogenized by heating at temperatures above that of the solvus and below that of the solidus (Bowen and Tuttle, 1950, p. 497), some of the samples containing two kinds of feldspar were tested by this means. Homogenization was nearly complete, except for a couple of modified albite peaks that persisted. From the position of the 201 peak, apparent compositions ranged from about Or<sub>25</sub> to Or<sub>45</sub>. This test is not definitive, however, because it was found that finely ground mechanical mixtures of orthoclase and albite, treated in the same manner, react similarly.

#### QUARTZ AND MICROCRYSTALLINE QUARTZ

Quartz occurs in all beds, and microcrystalline quartz in many beds, of the section. The total amount of quartz and microcrystalline quartz, as estimated from the chemical analyses, ranges from a few percent to about 50 percent. Microcrystalline quartz makes up only a small part of the total, although in beds P-16 and P-56 thin interbeds are composed almost entirely of microcrystalline quartz.

Most of the quartz occurs as discrete anhedral particles that tend to be equidimensional though subangular in shape, although some particles are lath shaped or splinterlike. The latter have a length-to-width ratio greater than about 3 to 1 and generally have extinction inclined to the long dimension. Weaver (1955, p. 168) suggests that lath-shaped quartz in some samples of the Phosphoria in Montana is of volcanic origin, and that the particles are similar to the quartz paramorphs after tridymite described by Ray (1947) and Wager and others (1953). Inclined extinction of these particles is similar to that shown by the quartz paramorphs, but inclined extinction also occurs where elongation is determined by the rhombohedral cleavage, the type of fracturing Ingerson and Ramisch (1942, p. 597) found was favored in some quartz-crushing experiments. Authigenic quartz crystals tend to be elongate owing to their strong tendency to occur in the prism form, but in which they exhibit parallel extinction. Organic quartz spicules and spines are nearly always composed of microcrystalline quartz in Phosphoria rocks. It thus seems that the lath-shaped quartz particles are either quartz paramorphs of volcanic origin or are fractured particles elongated in the direction of the rhombohedral cleavage. Data are insufficient at present to decide between the two possibilities.

Inclusions in quartz are common. Most of them are bubbles as much as several microns in diameter but generally about 1 micron or less. Their distribution is mostly irregular though some occur

along planes, giving a common bubble or dust-chain appearance. Carbonate occurs as apparent inclusions of varying amount in which it has replaced quartz. Illite is common as replacement inclusions in some beds. The iron oxide carbonaceous material occurs as inclusions around the border of some particles. Other less abundant inclusion minerals which occur are zircon and fine needles of rutile(?) (bed P-70).

Quartz, which occurs in very small veins in bed P-107 (pl. 30A), shows an unusual combination of properties. Its index of refraction is slightly less than that of canada balsam, and it shows strong irregular extinction like that of microcrystalline quartz; yet it has a good crystal outline. X-ray analysis verifies that it is quartz.

Microcrystalline quartz occurs mostly as matrix material intimately mixed with the iron oxide-carbonaceous material and the clay minerals. Discrete particles or masses in such occurrences of microcrystalline quartz are difficult to define, and estimates of their amount cannot be made from thin section. However, in some carbonate rocks, it forms small segregations of irregular form. In these carbonate rocks the refractive index of the microcrystalline quartz is less than that of canada balsam.

Microcrystalline quartz is typically full of bubbles, though the concentration of bubbles is variable. The bubbles are believed to be liquid-filled cavities as shown by their moderate relief and low refractive index with respect to quartz. The refractive index of the microcrystalline quartz is distinctly less than that of canada balsam in some occurrences and slightly greater in others. Folk and Weaver (1952) show that the lowering of the refractive index of microcrystalline quartz with respect to normal quartz is a direct function of the abundance of liquid-filled cavities in the microcrystalline quartz.

#### MICA GROUP

Muscovite and biotite are the mica minerals present in the section. Two petrographic types of muscovite, defined somewhat arbitrarily on the basis of size and mode of occurrence, probably represent at least two of the polymorphs of muscovite determined by Yoder and Eugster (1955). Although fine fractions of the samples have not been sufficiently pure to identify the polymorphs by X-ray methods with precision, the muscovite in the clay fraction of a sample from bed P-101 apparently consists mostly of the 1Md polymorph, or what is here called illite, a very fine size mica. The differential thermal-analysis pattern is characteristic also of illite. The other petrographic type, present as large laths, is probably a different muscovite polymorph; but in the absence of more specific identification, it is called simply muscovite in further descriptions.

Muscovite has been identified in nearly all the beds of the section. It occurs as discrete laths that commonly are 0.05 to 0.15 mm in length and that have a length-to-thickness ratio of about 10:1. Cleavage lines are generally well expressed and the laths show various degrees of "freshness." Some are sharply rectangular with straight regular borders and others are irregular and ragged, particularly at the ends of the laths. It is not uncommon to find laths that have been bent or broken during compaction of the sediment (pl. 30*B*). Strain developed at the points of bending results in the lowering of interference colors and irregular extinction. Inclusions are common and are mostly iron oxide-carbonaceous material that occurs along cleavage planes or along the margin of the laths. Other inclusions are carbonate and in one instance zircon. The bent and broken laths and the zircon inclusions in one particle suggest that the muscovite is exogenic.

Illite is the very fine grained mica that occurs in and makes up a considerable part of the matrix. Generally it is so intimately mixed with iron oxide-carbonaceous material and microcrystalline quartz that its character is largely indiscernible; in aggregates, however, its characteristic relief and interference colors are distinctive. In contrast to muscovite at least part of the illite is autigenic, as shown by its development in and along the margins of quartz and feldspar particles.

Biotite is scarce, at least in its recognizable form. In the three samples from beds P-3, P-82, and P-99, in which biotite was found, it is strongly altered. The biotite is believed to be of volcanic origin and indicative of the occurrence of an unknown amount of pyroclastic material in the section. This interpretation is based on a review of descriptions of tuff and bentonite which show that the occurrence of biotite is nearly ubiquitous. In addition, because of its poor resistance to weathering, biotite is commonly found only in rapidly deposited sediment, such as graywacke and arkose. Biotite has been found in the Phosphoria at one other locality—the Kelly Gulch section in southwestern Montana (Weaver, 1955, p. 172).

#### KAOLIN GROUP

The name kaolinite is used in the broad sense to include that group of clay minerals, other than the chlorites, which show the typical X-ray basal (001) reflection with a spacing of about 7.15 Å. It occurs in many of the beds in the section but only in very small amount. In this section Kaolinite is easily recognized by its characteristic occurrence as "books" of medium relief and by its low interference colors. In one bed several "books" are aligned end to end in such a way as to suggest that they had been derived from muscovite. In

other places kaolinite is found as relatively large aggregate particles.

It is noteworthy that illite and kaolinite are the only clay minerals which have been identified in this section of the Meade Peak member, although it is possible that small amounts of others were overlooked. Mixed-layer illite-montmorillonite has been found in one sample at Trail Canyon, Idaho; and G. A. Herr<sup>3</sup> found this to be common in some samples from Montana; montmorillonite has been also identified in samples of the Phosphoria in Montana by Weaver (1955, p. 175), L. F. Rooney,<sup>4</sup> and Herr.

### IRON SULFIDES

Pyrite has been identified only in beds P-71 through P-75, the "vanadiferous zone," which contain more sulfur than do any other beds in the section. Pyrite probably occurs in small amount in most of the other beds, although it has not been detected. The samples from the "vanadiferous zone" that were taken from an adit are unweathered, but the other samples contain iron oxides that probably have been derived in large part from pyrite by weathering. The pyrite in the "vanadiferous zone" was detected by X-ray methods. It is not identifiable in thin section but apparently comprises part of the black opaque amorphous-appearing matrix, presumably an intimate mixture of carbonaceous material and sulfide. Another sulfide mineral may be present in the rocks of this zone, since hydrogen sulfide is evolved when a sample is treated with hydrochloric acid. Pyrite and marcasite are unaffected by the acid, but pyrrhotite or a simple iron sulfide would produce such a reaction. Pyrrhotite is an unlikely constituent of these rocks. More likely the material is similar to that found in some modern marine sediments by Emery and Rittenberg (1952, p. 791), which reacted with hydrochloric acid, and which they suggest is hydrotroilite ( $\text{FeS} \cdot n\text{H}_2\text{O}$ ) or melnikovite (a cryptocrystalline  $\text{FeS}_2$ ). Another possibility is that the acid reacted with sulfur-containing organic compounds rather than with iron sulfide.

### IRON OXIDES

Identification of the iron oxide minerals is possible only in a general way because of their particulate state. An exception is the iron oxide occurring as small globules, commonly in swarms in which some of the globules are spherical. These globules are blood red or opaque in transmitted light, blood red in reflected light, and have high relief. Other optical properties cannot be determined because of the small

<sup>3</sup> Herr, G. A., 1955, Clay minerals in the Phosphoria formation in Beaverhead County, Montana: Indiana Univ. thesis.

<sup>4</sup> Rooney, L. F., 1956, A stratigraphic study of the Permian formations of part of southwestern Montana: Indiana Univ. thesis.

size of the globules and their strong coloration, but the observable properties suggest that the mineral is hematite, or possibly goethite.

The iron oxide occurs mostly as finely disseminated brown particles mixed with black organic material. It is designated as limonite in the broad usage of the term, which includes all the hydrous or hydrated iron oxides. Iron oxide is ubiquitous and, along with the carbonaceous material, is responsible for the coloring of the rocks.

#### OTHER SULFUR COMPOUNDS

Sulfur occurs in several ways in these rocks. As described previously, it occurs in pyrite and possibly as a simple iron sulfide; and it is believed to occur in apatite diadochic with phosphorus. Some probably occurs in organic compounds that compose the carbonaceous material in the matrix. Some occurs as gypsum in the weathered rock of the "vanadiferous zone" and is derived presumably by the oxidation of pyrite.

#### CARBONACEOUS MATERIAL

Little is known of the chemical character of the carbonaceous material, though part of it is bituminous as indicated by its odor. Sulfur is undoubtedly a component of the carbonaceous material, but it is not known how much occurs in organic compounds as compared with iron sulfides. The carbonaceous material is black and opaque where concentrated but brown where disseminated. To rocks it imparts a blackness, which is a rough indication of the amount of carbonaceous material present. The carbonate rocks contain the least carbonaceous material and are, therefore, generally the lightest in color.

#### ACCESSORY MINERALS

Fluorite, titanite, leucoxene, tourmaline, and zircon are common but minor constituents of the rocks. Fluorite occurs mainly in phosphorite. A single occurrence was found in dolomite in bed P-42. In phosphorite it occurs both within and among carbonate-fluorapatite pellets.

Titanite is relatively abundant. Its high interference colors, high relief, and strong dispersion are distinctive. A white semitransparent substance is believed to be leucoxene. Tourmaline is less abundant than titanite; it generally is brown but some is green or grayish blue. Tourmaline ranges from irregularly shaped to subhedral particles. Zircon occurs in its typical rounded prismatic form.

#### PETROGRAPHY

##### ROCK TYPES

Rocks of the Meade Peak member are of three principal end-member types—carbonate rock, phosphorite, and quartz-silicate rock. In



general, their physical character is similar. All are fine grained, except those phosphorites that are composed of sand-sized pellets and oolites. All are dark colored—black and dark shades of gray and brown; in order of darkest to lightest they are some of the quartz-silicate rock, phosphorite, and carbonate rock. All are thin bedded so that they are measured in tenths of a foot, except for some carbonate-rock beds that are a foot or more in thickness. Most of the rocks weather to small thin plates, but some of the carbonate rocks and phosphorites weather into small irregularly shaped chunks.

#### COMPOSITION

Carbonate rock is composed largely of dolomite and calcite, and for specific purposes is subdivided into dolomite and limestone. Phosphorite is composed predominantly of carbonate-fluorapatite. The quartz-silicate rock is composed largely of quartz, feldspar, muscovite, illite, and kaolinite. Because the amounts of these latter constituents have not been determined individually, their group total is represented by the acid-insoluble chemical determination (table 1). The acid-insoluble determination involves solution, oxidation, and strong ignition of the rock, so that only the very resistant quartz and silicate minerals remain in which there is some loss in solution and ignition, presumably from muscovite, illite, and kaolinite. This loss is indicated by the fact that the acid-insoluble totals about 2 percent less than do the main silicate constituents,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , in the 15 rocks with the highest quartz-silicate content. This figure does not include structural or absorbed water lost in ignition above  $105^\circ\text{C}$ . Thus the quartz-silicate content of the rocks as represented by the acid-insoluble determinations (table 1) is, in general, a minimum value.

#### RANGE OF MIXTURES OF END-MEMBER ROCK TYPES

Only the end members have been considered up to this point; but in order to show the relationship of their characterizing mineral components in all the rocks of the Meade Peak member, the components are plotted on a ternary diagram in figure 10. The three components—carbonate (calcite plus dolomite), carbonate-fluorapatite, and quartz-silicate—have been recalculated to represent 100 percent for all beds of the section not composed of interbedded lithologic units.

As can be seen in figure 10, the rocks tend to cluster toward the apices of the triangle; that is, rocks in which one end member is dominant are more common than those of intermediate composition. The quartz-silicate component mixes with carbonate and carbonate-fluorapatite in about all proportions. However, the mixing of carbonate and carbonate-fluorapatite appears to be restricted; the two

components do not tend to occur with one another in proportions of less than about 3:1. Such a restriction is indicated not only by the left-central barren part of figure 10 but also by the lack of rocks that would compositionally fall in the central part of the triangle. The relationship between the carbonate minerals and apatite in the rocks is described further on in this report.

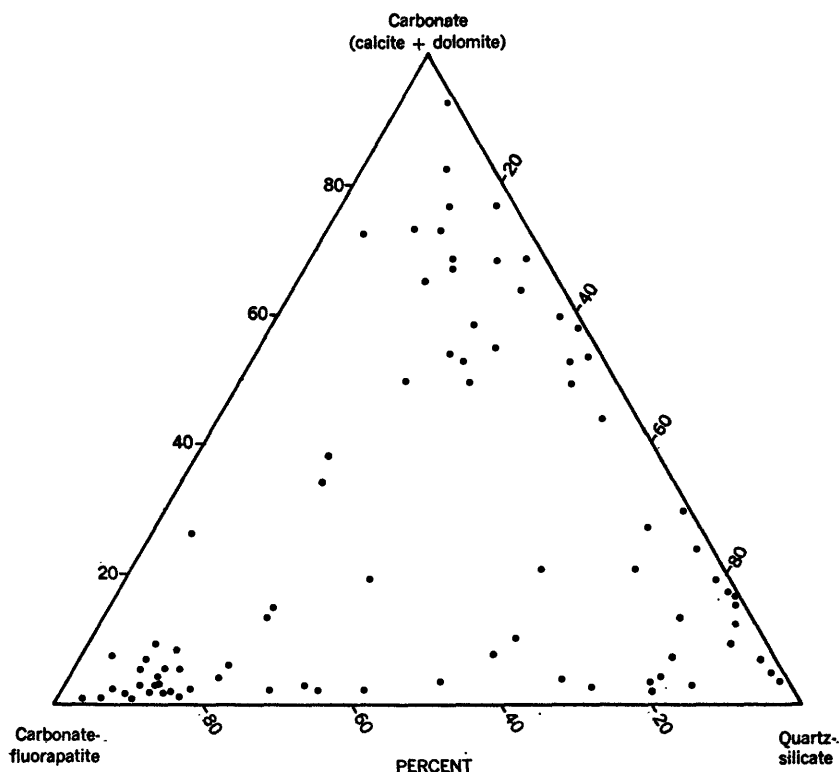


FIGURE 10.—Ternary plot of principal mineral components representing end member rock types, recalculated to 100 percent of all beds except those composed of interbedded lithologic units.

## CARBONATE ROCK

### PETROGRAPHIC TYPES OF CARBONATE

The dominant mode of occurrence of the carbonate minerals is as subequidimensional, anhedral, inclusion-filled, pale-brown particles. Variation from this type of carbonate is marked but continuous, and cannot be distinctively categorized, except for the carbonate which has filled fractures, replaced quartz, feldspar, and muscovite, and that which constitutes fossil shells or shell fragments. Vein and replacement carbonate differs from the modal type carbonate in that it is colorless and is relatively free of inclusions. The carbonate from

shells of Foraminifera and shell fragments of brachiopods or pelecypods is fine grained and has a distinctive shape and structure. The fossil makes up a very small proportion of the total carbonate.

#### TEXTURE

Carbonate rocks are composed of particles or grains of carbonate and other minerals that produce a granular texture (pl. 31A). There is virtually no matrix. The size and shape of the carbonate particles are frequently difficult to determine because their physical boundaries are often discontinuous or indistinct; also particles defined largely by physical boundaries may not be homogeneous with respect to optical properties. In contrast, carbonate microfossils and fossil fragments, which occur in significant amount in some of the rocks, are sharply defined.

Most of the carbonate particles range from 20 to 60 microns in diameter. The smallest particles that can be resolved are about 2 microns, and the largest carbonate particle found, not including shells or shell fragments is about 300 microns. The size distribution is approximately seriate with a single mode. An exception is the relatively large phenocrysts in bed P-42 which set in a much finer grained matrix with few, if any, intermediate-sized particles. A few beds show a marked uniformity of size; that is, a small size range and a distinct modal group, analogous to that in well sorted beds of detrital material.

Both dolomite and calcite occur most commonly as subequidimensional anhedral particles reflecting their tendency to crystallize as rhombohedrons. Calcite particles, which vary from the subequidimensional anhedral form, tend to be more irregular and larger; and dolomite particles, more euhedral and larger. Shell material contributes to the irregular shape of some calcite; however, the irregular shape of other calcite, as that in bed P-66, is due to secondary growth which has resulted in the incorporation of other mineral particles within the calcite particles. Rhombohedrons of dolomite are not common but are striking in their appearance, as is shown in plate 31B in which the rhombohedrons resemble phenocrysts, much larger than any of the surrounding particles. In bed P-56 (pl. 32A) the dolomite has been reorganized into large subhedral particles whose unequal development is the result of mutual interference in their growth.

The carbonate-rock texture reflects two main stages of modification of a primary accumulation of very small particles: aggregation and primitive reorganization, and advanced reorganization.

During aggregation and primitive reorganization, the physical boundaries of the particles are vague and discontinuous, and groups of particles have attained a degree of optical homogeneity. Particles

separated by a physical boundary may have nearly the same optical orientation. This gives rise to the common phenomenon of migrating extinction in which the darkness of extinction passes uniformly from particle to adjacent particle, indicating a gradual change in the orientation of the particles not affected by apparent physical discontinuities. This phenomenon is interpreted to indicate that reorganization of the carbonate particles has occurred, but in which particle growth, apparently by accretion of adjacent particles, is imperfectly attained.

Advanced reorganization of the carbonate particles is indicated by an increase in particle size; by a tendency for euhedral development, except where the particles mutually interfere in their growth; and by the attainment of the greatest degree of physical and optical homogeneity of all the carbonate particles. Some iron oxide-carbonaceous material occurs as relatively large segregations within the particles or in concentrations along their borders, a mode of occurrence that indicates a tendency by the particles to exclude foreign particles during their reorganization.

#### INCLUSIONS

Inclusions in dolomite and calcite particles are common and generally abundant. Most of the carbonate particles are aggregates and, in those composed of one large and several small particles, the small particles may be considered as carbonate inclusions. In addition to carbonate inclusions, there are generally many bubbles (presumably liquid inclusions) and a very finely divided dark-brown material believed to be mostly iron oxide-carbonaceous matter and, more rarely, brown isotropic carbonate-fluorapatite. The dark-brown material is always present but varies considerably in amount. It imparts the coloration to light-brownish carbonates. Where it occurs in large amount, the nature of the carbonate is obscured to a considerable degree. Where it occurs in small amount and is finely disseminated throughout the carbonate, the color is hardly perceptible except where contrasted with clear, colorless vein calcite.

Only in bed P-66 have other minerals occurred as inclusions in the carbonate. Here large irregular masses of reorganized calcite enclose quartz, feldspar, and muscovite particles.

#### REPLACEMENT

Carbonate replacement of other minerals seems not to have occurred on a large scale. In bed P-80, however, calcite replaces brown isotropic carbonate-fluorapatite. Relict pelletal outlines are preserved, and some ragged apatite masses occur as nuclei within the relict pellets. The replacement calcite within the relict pellets is strongly brown-colored as compared to the calcite enclosing them.

Carbonate replacement on a small scale has occurred in nearly all

beds. Carbonate commonly replaces quartz as projections and embayments along the boundaries of the quartz particles. Feldspar and muscovite have been replaced by carbonate in the same manner but not as frequently. The carbonate replacing these minerals is colorless and stands out sharply in contrast to the modal carbonate.

Replacement of carbonate has been noted in only one bed, P-56, where microcrystalline quartz has replaced the corner of a dolomite rhombohedron and whose outline has been preserved.

#### CLEAVAGE AND TWINNING

Cleavage is weakly developed and is generally found in only the larger carbonate particles. Twinned particles are uncommon in the section as a whole but are abundant in some beds, such as P-28 and P-79.

#### PHOSPHORITE

##### PETROGRAPHIC TYPES OF CARBONATE-FLUORAPATITE

Most of the carbonate-fluorapatite is submicrocrystalline, brown, inclusion filled, and optically isotropic. Light-brown anisotropic apatite occurs as layers on oolites that show the extinction cross, indicating a radial orientation of the crystallites in the layers. Most fish scales and fragments of bone and (or) tooth are also composed of anisotropic apatite, and orientation of the crystallites, although not radial, is indicated by wavy extinction. Other fossil fragments contain colorless apatite, probably owing to recrystallization. Colorless and inclusion-free anisotropic apatite frequently occurs as small segregations in pellets and oolites. Euhedral apatite crystals have been found in veins in the phosphorite and in one specimen in a matrix of microcrystalline quartz (pl. 32B).

#### TEXTURE

The two principal textures of the phosphorite can be described by the terms "microphanite" and "pelletite," both of which are used in a rock classification by V. E. McKelvey, R. A. Gulbrandsen, and R. P. Sheldon (written communication, 1958) of the U.S. Geological Survey. Microphanite is composed mainly of an interlocking mosaic of sutured subhedral or euhedral crystals less than 0.0625 mm in diameter. Although the apatite microphanite considered here is composed of submicrocrystalline particles, there can be little question but that the relationship between the individual crystallites is undoubtedly of the kind described in the definition of microphanite. Pelletite, as shown in plate 33A, is composed mainly of well-sorted spherical or subspherical aggregates that have no internal structure and that have a modal diameter of 0.0625–2.0 mm. Oolite, plate 33B, is the equivalent of pelletite, except that the aggregates have a concentric

internal structure. Only in beds P-1 and P-97 is the oolite texture predominant. Pelletite is a more common texture than is microphanite. Phosphorite may contain only pellets, but that which contains oolite grains contains pellets too. Mixtures of microphanite with pelletite and oolite occur in many beds; but where microphanite is in small amount, it is considered to be cement. Pellets are indistinct in some phosphorite, representing a texture intermediate between microphanite and pelletite; such incompletely developed aggregates are called incipient pellets.

Almost all the carbonate-fluorapatite is submicrocrystalline. The remainder is macrocrystalline and consists of small anhedral to euhedral crystals. Pellets and oolites, which are aggregates of submicrocrystalline apatite, range from spherical to markedly elongate shapes. Those that are elongate have their axis of elongation remarkably parallel in some beds but not in others. The pellets and oolites are well rounded, even those whose outline is irregular. Both pellets and oolites are generally much larger than other mineral particles in a bed. For the member as a whole, their modal size ranges from about 0.1 to 0.5 mm in diameter, and the maximum is about 5.0 mm. Fish scales and fragments of bone and tooth commonly are measured in tenths of a millimeter.

#### INCLUSIONS AND COLOR

Some pellets and oolites may contain inclusions of one or more of the major minerals in the rocks, but most contain few or none. Small segregations of colorless anisotropic apatite are common, but few occur within one pellet or oolite. Some fluorite is present in this manner also. Nuclei of fish scales and bone or teeth fragments in the aggregates are scarce except in bed P-1.

The submicrocrystalline apatite ranges from light brown to very dark brown. The coloration is commonly splotchy and is due to the presence of finely divided iron oxides and carbonaceous material. Upon heating the apatite to 1,000°C most of the brown color and carbonaceous material is lost, leaving only reddish-brown iron oxide as a residue of the included material.

#### DEVELOPMENT OF PELLETS AND OOLITES

Apatite microphanite represents an unmodified accumulation of apatite. A postdepositional formation of aggregates from such a primary accumulation of apatite is indicated in those rocks that show incipient pellets. Complete pelletization is not recognized with certainty, but some of the pelletites that do not show evidence of pelletization prior to deposition may be of this derivation. Pelletization prior to deposition is indicated by the presence of pellets in

carbonate and quartz-silicate rocks; by the occurrence of quartz and silicate minerals interstitially to pellets that do not contain those minerals as inclusions; and by the occurrence of apatite cement between the pellets.

The development of oolites is not well understood and only a few observations about them are made here. The oolites are not completely layered from their centers to edges, indicating that they all must have nuclei, even though most of the nuclei consist of structureless apatite. Other less common nuclei are organic apatite fragments and, rarely, quartz grains. The oolites most likely formed prior to their final deposition, and they probably have a complex or varied earlier history of formation. Formation of the remarkably uniform and delicate layering probably required that the entire surface of an oolite be free to accrete new material evenly and essentially simultaneously. Growth while the oolite was spinning in suspension or rolling gently on the bottom may be the explanation, but it is difficult to conceive of how uniform layering, concordant with the irregular shape of some of the oolites, could form in this manner, particularly by a bottom rolling mechanism. It may be that the layers of oolites are not accretionary but result from reaction and recrystallization of the outer part of the pellets, as suggested by Lowell (1952, p. 35).

#### QUARTZ-SILICATE ROCK

Quartz-silicate rock contains two elements of texture, grains and matrix. The grains are composed dominantly of quartz, feldspar, and muscovite; and the matrix is composed largely of illite and some microcrystalline quartz mixed with iron oxide-carbonaceous material. The matrix materials are very finely divided and intimately mixed. They vary in amount to the extent that certain minerals dominate in particular samples; for example, rocks of the vanadiferous zone in beds P-71 to P-75 contain more carbonaceous material and fine pyrite than do the other rocks. Carbonate minerals and apatite occur in a wide range of proportions with the quartz-silicate constituents, as previously described. Apatite pellets are generally large relative to other grains of the quartz-silicate rock and produce a distinct bimodal-size distribution. Most of the grains range from 0.02 to 0.05 mm, coarse silt size. Muscovite occurs typically as lath-shaped particles that range in length from about 0.05 to 0.15 mm and have a length-to-thickness ratio of about 10:1. Quartz and feldspar tend to be equidimensional and subangular to subround; and both, but particularly feldspar, may be subhedral to euhedral. These minerals and other constituents in the quartz-silicate rocks are further described under "Mineralogy," beginning on p. 91.

### PETROLOGY

The constituents that compose the rocks of the Meade Peak member are broadly classed as exogenetic or endogenetic. Most of the quartz-silicate suite of minerals are exogenetic, derived principally as detritus but possibly, in part, as pyroclastic fragments. The occurrence of this mineral group is primarily the result of physical processes. The group of major constituents composed of apatite, dolomite, and calcite is endogenetic, and its occurrence is largely the result of chemical processes. The occurrence of these two groups was shown previously to be virtually independent of one another, and attention is directed here to chemical processes involved in the formation of the endogenetic group—apatite, dolomite, and calcite. Other endogenetic constituents, such as carbonaceous material, sulfide, some illite and feldspar, and many minor constituents, have been described to the extent possible at this time in previous parts of this report.

The chemical composition of the section of the Meade Peak member at Coal Canyon, as noted earlier, is unusual in that phosphorus and fluorine are abnormally abundant. These elements occur in carbonate-fluorapatite, which is the most abundant mineral in the member. Apatite is also one of a group of chemically related minerals—apatite, dolomite, and calcite—that comprises more than 50 percent of the total mineral composition. The occurrence of these three minerals in the rocks at this locality and the association of the minerals on a broader scale provide a basis for investigating their modes of formation.

### NATURE OF ROCK-TYPE CHANGES

The member is composed of three principal rock types, some of which contain large amounts of their characterizing minerals. The rock strata most commonly range from 0.5 to 2 feet in thickness and overlie each other in unsystematic alternation. As can be seen from the columnar section (pl. 28), there are 56 alternations or changes of rock type and 57 rock units (determined by grouping adjacent beds with the same rock name). The 13 quartz-silicate units do not appear to preferentially overlie or underlie either of the other types. The 23 carbonate units and 21 phosphorite units overlie one another about the same number of times. Also, there is no favored sequence or triplet of the three rock types. Where adjacent beds are of different composition, the difference is large. It is unusual for a group of beds to show uniform progressive change. Qualitatively the mineral composition of the Meade Peak member is the same throughout; the different rocks are due to different proportions of the major minerals. In addition, the number of major minerals is small. These features indicate that highly selective physical and chemical processes prevailed during the time that the rocks of the Meade Peak member were formed,



and that specific conditions prevailed for considerable lengths of time in order to produce the thickness of the individual rock units. These relationships provide no obvious key to the origin of the phosphorite and carbonate rocks, beyond indicating an intimate association of the rock types; but the features conform, in general, to a hypothesis explored here which considers the relation of vertical lithologic changes at a locality to lateral changes or facies of rock units.

#### **RANGE AND DISTRIBUTION OF CALCIUM**

Apatite, dolomite, and calcite are chemically related minerals that have two ions in common: the calcium and carbonate ions. Although carbonate occurs in the apatite in only small amounts, calcium is a major component of all three minerals and is the most abundant oxide (27 percent CaO) of all the constituents in the member as a whole. A frequency diagram (fig. 11) shows that the CaO content is virtually symmetrically distributed with one distinct mode. This signifies that calcium was supplied continuously and uniformly as sediment in one or more of its three mineral phases, and that the amount concentrated at any one time was dependent upon the amount of dilution by quartz-silicate detrital material. Thus the modal class of calcium concentration represents the most common or prevalent condition, and variation from that to the right are toward greater concentration of calcium minerals and to the left toward lesser concentration and greater dilution by detrital minerals. The type of calcium mineral that formed at a particular time depended essentially upon the effective concentration of magnesium and phosphate ions in the marine water.

#### **MIXTURES OF APATITE, DOLOMITE, AND CALCITE**

Apatite, dolomite, and calcite occur in the member as mixtures of one with another (binary mixtures) or all together (ternary mixtures). Apatite occurs virtually alone in a few of the rocks. In figure 12 the percentages of the three minerals, recalculated to equal 100 percent, are plotted on a ternary diagram for all beds of the section in which the three minerals total more than 50 percent and which have virtually a homogeneous composition. The 50 percent cutoff is designed to exclude samples in which modifications resulting from secondary processes, such as diagenesis and weathering, would be proportionately greater and would tend to obscure primary compositions. Calcite that occurs along fractures and joints is a contaminant of this kind. The samples selected here only approximate an ideally homogeneous rock; and, therefore, the rocks are not precise representatives of discrete primary mineral mixtures. It is not likely, however, that the effects owing to incomplete homogeneity

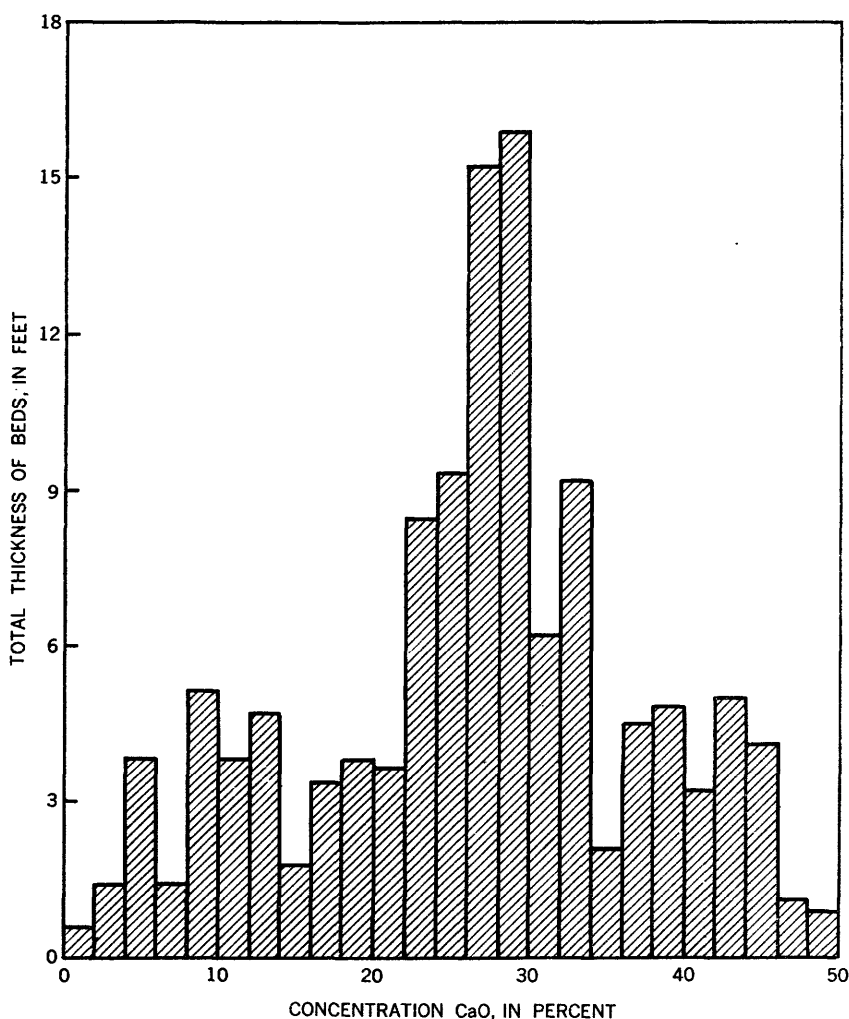


FIGURE 11.—Graph showing frequency of occurrence of CaO in all beds of the Meade Peak phosphatic shale member.

of the rocks and to secondary processes are large enough in most rocks to obscure primary relationships entirely.

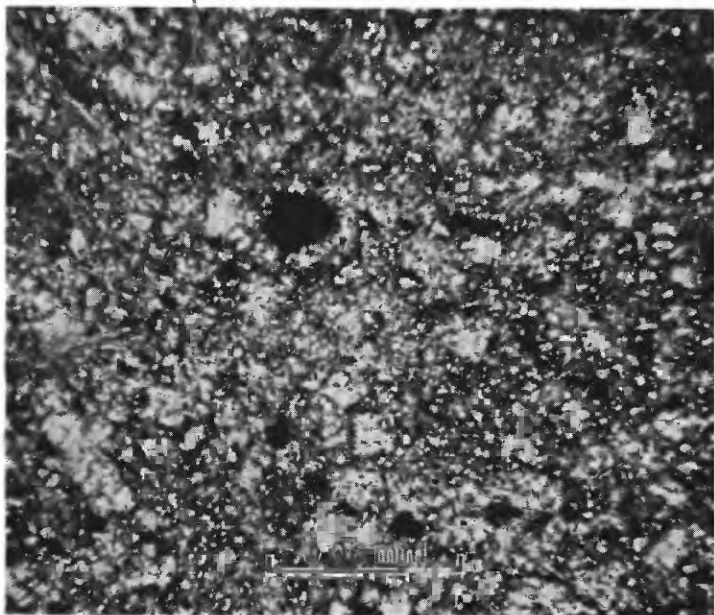
The samples shown in figure 12 are distributed along the dolomite-apatite and dolomite-calcite edges of the triangle. There are two principal groups of samples. Samples of the larger group are composed mostly of apatite, and samples of the other group in the dolomite corner are mostly dolomite-apatite mixtures. Samples distributed along the dolomite-calcite edge cover nearly the entire range of dolomite-calcite proportions. The near absence of points along the



A. QUARTZ CRYSTAL IN VEIN IN CARBONATE ROCK FROM BED P-107  
Its index of refraction is less than that of balsam, and it shows strong irregular extinction.

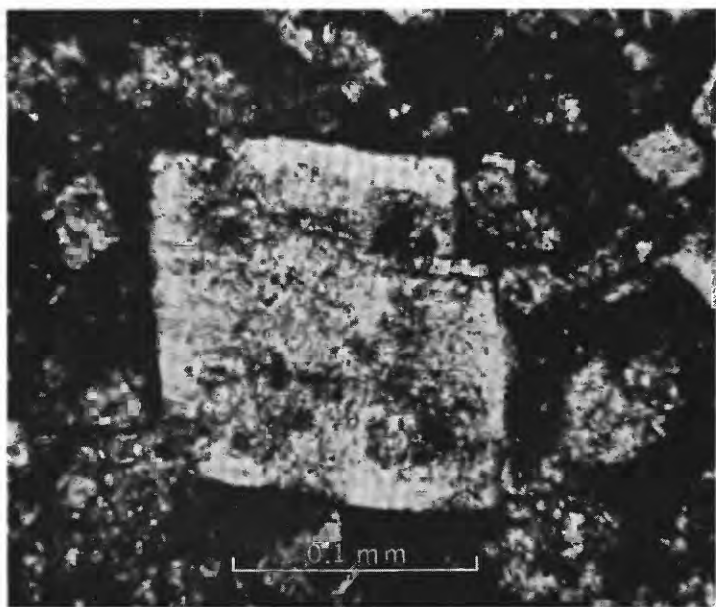


B. BENT MUSCOVITE IN CARBONATE ROCK FROM BED P-99  
Marked strain shadows shown by upper lath where bent.



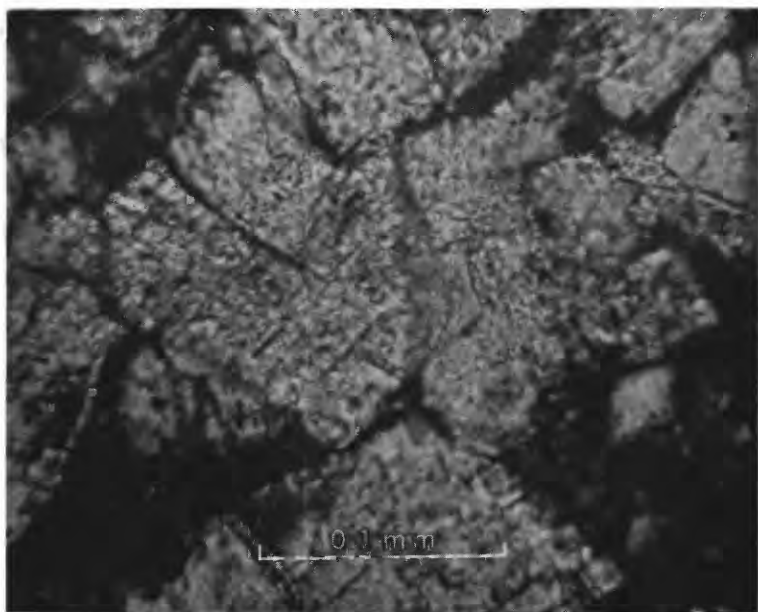
A. GRANULAR TEXTURE OF CARBONATE ROCK IN BED P-107

The particles that make up the rock consist of 51 percent dolomite and 22 percent calcite.



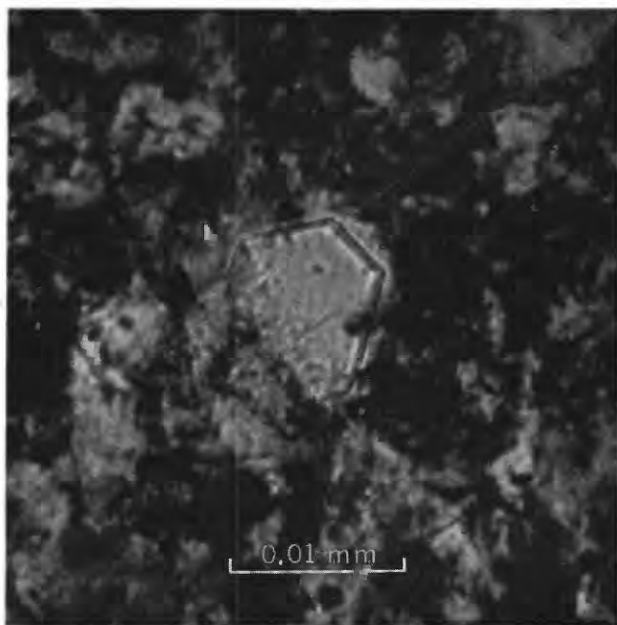
B. DOLOMITE PHENOCRYST SET IN A FINE-GRAINED MATRIX OF CARBONATE AND DARK-BROWN MATERIAL

Note that both the phenocryst and the smaller carbonate particles contain many dark-brown inclusions.



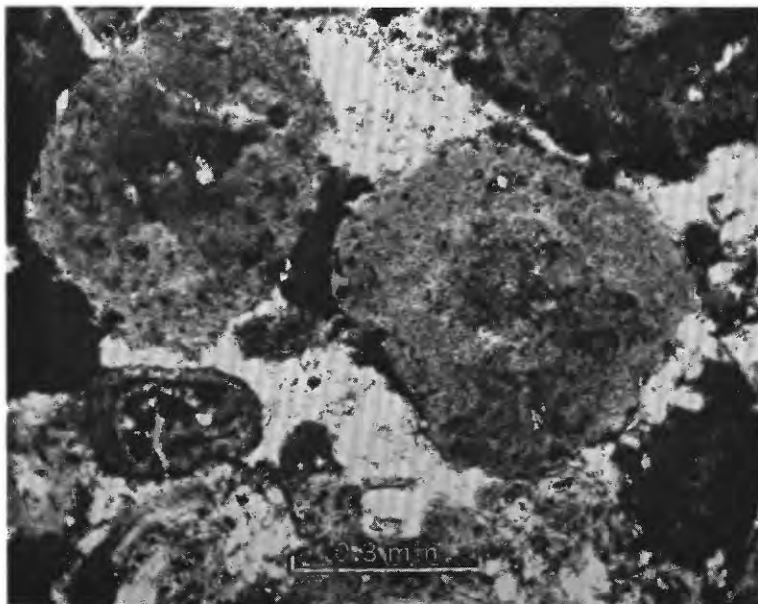
A. SUBHEDRAL DOLOMITE CRYSTALS FROM BED P-56, SHOWING MUTUAL INTERFERENCE IN THEIR GROWTH

Note that the crystals contain many inclusions.

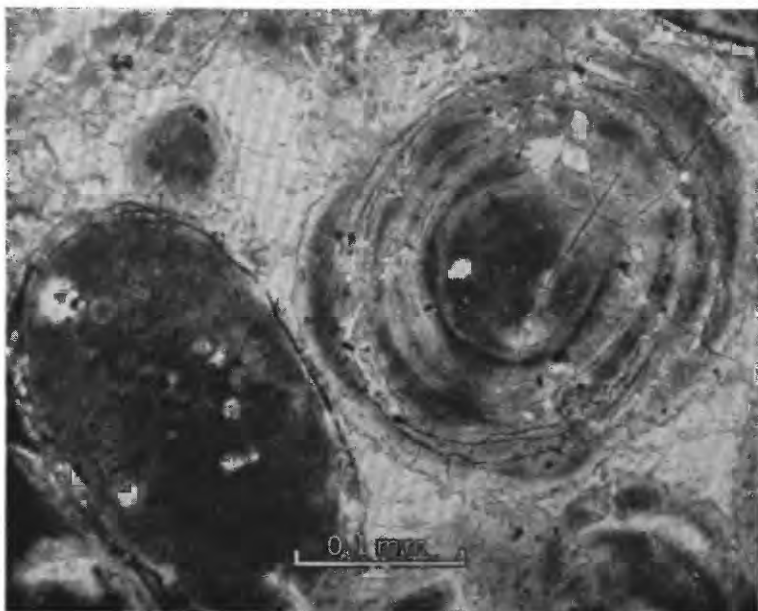


B. CARBONATE-FLUORAPATITE CRYSTAL FROM BED P-16

The matrix consists of microcrystalline quartz, iron oxide, and carbonaceous material.



A. APATITE PELLETS IN PHOSPHORITE IN BED P-85  
White interstitial material is calcite and quartz grains.



B. APATITE OOLITES IN PHOSPHORITE IN BED P-97  
Interstitial material is carbonate and apatite.

calcite-apatite edge and in the central part of the diagram suggests that there is an antipathetic relation between calcite and apatite. The two groups of samples, which include a majority of all the samples, represent the dominant types of mineral associations in the section. The dolomite-calcite mixtures represent the only other principal mineral association, but they cover a large range of mineral proportions.

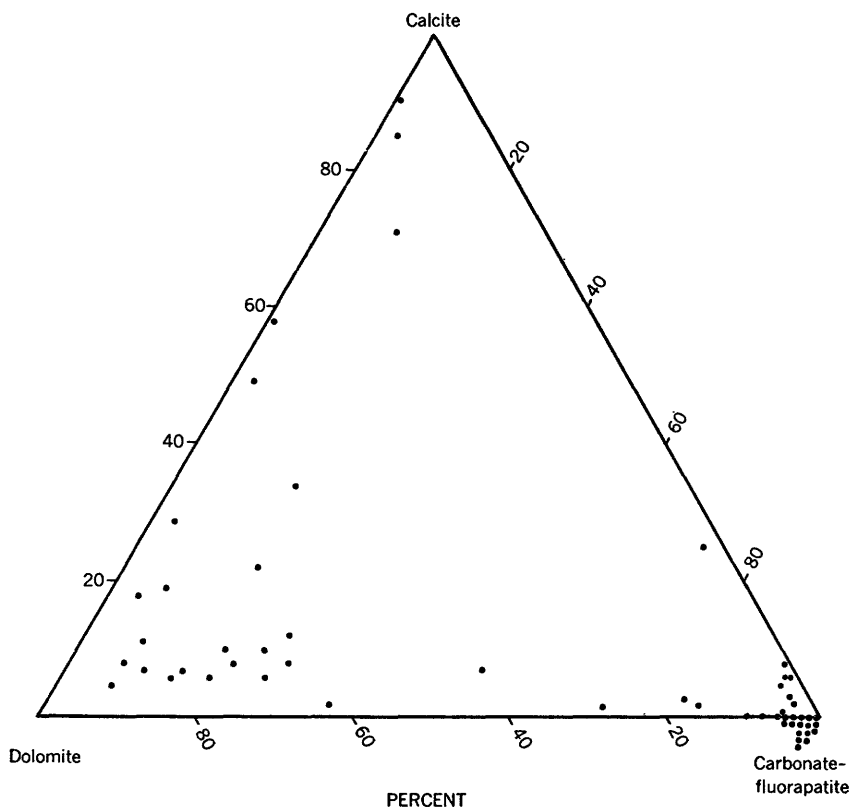


FIGURE 12.—Ternary plot of the percentages of calcite, dolomite, and carbonate-fluorapatite, recalculated to equal 100 percent, of all beds in which the three minerals total more than 50 percent and which are not composed of interbedded lithologic units.

#### BROADER RELATIONSHIPS OF MINERAL ASSOCIATIONS

All the features of the member just described are concerned with differences of mineral phases; and a hypothesis explored here attributes these differences to compositional changes of sea water. The feasibility of this hypothesis, although considered here only with respect to the section of the Phosphoria formation at Coal Canyon, is indicated also by some aspects of the overall mineral associations of the Permian rocks in Idaho and Wyoming. Facies changes east-

ward from southeastern Idaho to central Wyoming, with respect to the constituents of concern here, are from phosphorite to carbonate to anhydrite. If this is actually a continuous series, as stratigraphic data indicate, it might have resulted from a continuous eastward increase in salinity, or a salinity gradient, of the Permian sea. Thus Scruton (1953, p. 2506) ascribes the possible formation of lateral facies of carbonate, anhydrite, and salt to a salinity gradient; and C. U. Campbell<sup>5</sup> considers this hypothesis as a possible explanation of the carbonate to anhydrite facies change of the Permian rocks in the Bighorn River basin of north-central Wyoming. A real genetic relationship between phosphorite, carbonate, and anhydrite facies, which all have calcium as a common ion of their characterizing minerals, is suggested further by the fact that the Permian phosphorites of the Ural Mountains region of Russia have carbonate and gypsum facies (Kazakov, 1938). The occurrence of phosphorite and gypsum in Jurassic deposits in Mexico (Rogers and others, 1956, p. 85), in Cretaceous-Tertiary deposits in the Atlas Mountains of North Africa (Visse, 1952, p. 17, 20), and in Upper Cretaceous deposits in Israel (Bentor, 1953, p. 97) may be additional examples, but the facies relationships of these deposits are unknown. Only phosphorite and carbonate facies occur in Coal Canyon; so these are the only facies treated here.

#### **BASIC HYPOTHESIS OF THE FORMATION OF DOLOMITE, CALCITE, AND CARBONATE-FLUORAPATITE**

As a basic hypothesis, the occurrences of dolomite, calcite, and carbonate-fluorapatite in the rocks of the member are considered to represent approximately the solid phase or phases of these minerals in equilibrium with the sea water from which they formed. The three minerals are chemical compounds that have two ions in common; therefore, the conditions for the formation of the minerals must be interrelated. Thus the carbonate rocks and phosphorites represent accumulation of primary precipitates whose mineral proportions are due to the specific conditions prevailing at any one time. The proof of such a hypothesis must show, as a minimum requirement, that the occurrence of the minerals singly or as mixtures is possible theoretically and with respect to pertinent experimental data. The hypothesis assumes that equilibrium conditions were attained between sea water and the minerals formed from it. Common experience, however, has shown that in low-temperature reactions, such as those considered here, equilibrium is frequently not attained and that unstable or metastable compounds are formed;

---

<sup>5</sup> Campbell, C. U., 1955, The Phosphoria formation in the southwestern Big Horn Basin, Wyoming: Stanford Univ. thesis.



for example, Brooks and others (1950) have shown that metastable phases of calcium carbonate and its hydrates are reproducible under some conditions. One kind of mineral association is reasonably explained in this manner, but equilibrium is implicit in the general hypothesis.

#### REQUIREMENT OF CIRCULATING SEA WATER

Dolomite, calcite, and carbonate-fluorapatite together make up more than 50 percent by weight of the total mineral content of the Meade Peak member; the carbonate minerals are about equal to the amount of apatite. Although carbonate minerals occur in large amount throughout the geologic column, apatite is relatively scarce. In order to emphasize the magnitude of the amount of phosphate in the Phosphoria formation as a whole, McKelvey, Swanson, and Sheldon (1953, p. 56) calculated that the formation contains about  $1.7 \times 10^{12}$  metric tons of  $P_2O_5$ ; an amount that is more than five times the  $0.32 \times 10^{12}$  metric tons of  $P_2O_5$  in the present-day total volume of ocean and sea water of  $1370 \times 10^6$  km<sup>3</sup> (Sverdrup and others, 1942, p. 15, 220). These figures show that oceanic circulation over a long period of time is a prerequisite to the deposition of such an immense amount of material, and that the total volume of oceanic waters, so to speak, must have passed over this locus of deposition many times in order to form the Phosphoria formation. The importance of oceanic circulation to the formation of large phosphorite deposits is recognized also by Kazakov (1937, 1938). He postulates that cold phosphate-rich upwelling currents become saturated and precipitate phosphate on shelf areas as the water's temperature and pH increase and its CO<sub>2</sub> content decreases upon rising to the surface.

#### ROLE OF ORGANISMS

Animals and plants play a dual role in the formation of rock, directly contributing skeletal and shell material as sediment and affecting the overall physical-chemical environment by their life process and decomposition after death.

As a whole, skeletal and shell material make but a small contribution to the carbonate rock and phosphorite of the Meade Peak member, but the amount is significant in some rocks, such as shell fragments in limestone beds and bone fragments, fish scales, and teeth in phosphate rock. Though some carbonate-shell material has been reorganized in various degrees, no large-scale reorganization of this kind is apparent in either the carbonate or phosphate rocks.

Organisms thus probably did not play an important direct role in the formation of the sediment of the Meade Peak but they may have played an important indirect one through their affect on the physical-

chemical environment. Phosphorus, carbon, and calcium, the major elements in the carbonate and phosphate minerals, are essential to the metabolism of animals and plants. These elements are extracted from sea water by organisms and returned after their death. Life abounds near the surface of the sea in water rich in nutrients, and carbonate and phosphate minerals might not form other than as hard parts of animals and plants; however, upon death the elements are returned to solution and conditions may become favorable for precipitation of the minerals. Probably the best known hypothesis for the origin of the phosphate in the Phosphoria formation is the one proposed in detail by Blackwelder (1915) in which precipitation of phosphate results from the dissolution of phosphate from masses of animals killed in a catastrophe. An excellent large-scale study of mass mortalities associated with "red tides" by Brongersma-Sanders (1948) lends credence to the possibility that such a mode of formation may be significant in the origin of some phosphate.

The physical-chemical conditions of sea water, however, are basic to the formation of the carbonate and phosphate minerals, regardless of the indirect or intermediate role of animals and plants. And it should be noted, too, that the minerals composing the hard parts of plants and animals are closely similar to the minerals that are formed as precipitates. Thus the basic hypothesis proposed in this study for the formation of the carbonate and phosphate minerals applies, in general, to the mode of origin of both the organic material and precipitate.

#### **DOLOMITE-CALCITE-CARBONATE-FLUORAPATITE-SEA WATER SYSTEM**

Experimental study of the dolomite-calcite-carbonate-fluorapatite-sea water system, as a whole, has not been done; and most of the available data that pertain to the system only treat relationships of the individual minerals with the sea water. Inferences made here about the system are based on mineral solubilities, the nature of general phase relations, and indicated phase relations in the rocks of the Meade Peak member.

As an approximation, sea water is treated as a single component. Although the chemistry of sea water is complex, its gross effect upon the formation of dolomite, calcite, and carbonate-fluorapatite is considered constant. In general, sea water is remarkably uniform in the proportion of its dissolved constituents but varies significantly in its total salinity (Sverdrup and others, 1942, p. 166; Rubey, 1951, p. 1125). Average sea water (Rubey, 1951, p. 1126) at 8°C has a salinity of 35 g per kg. Deviation toward higher values that have been observed in today's oceans and connecting seas are as much as 35°C for tem-

perature and 42 g per kg for salinity (Emery, 1956, p. 2359, 2361), although the extreme surface salinity in the oceans proper is only about 37 g per kg (Sverdrup and others, 1942, p. 126). Even though the variation of salinity is not large, Trask (1936) found that the formation of calcium carbonate was favored in ocean water that had a high salinity content. Larger changes in composition are postulated for Permian sea water in this investigation of the formation of apatite and the carbonate minerals, and are indicated to have occurred in the extreme case by the large-scale formation of gypsum and anhydrite on the east side of the basin.

#### SOLUBILITY OF CALCITE

The solubility of calcite has been studied extensively. Miller (1952), in an excellent general study, has reviewed nearly all the significant earlier solubility determinations. He suggests that failure to control carefully the  $\text{CO}_2$  concentration accounts for many of the discrepancies in calcite solubility data. Miller (1952) and Faust (1949) have summarized the most recent data bearing on part of the system  $\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ .

Some of the more comprehensive and important theoretical and experimental work on the solubility of calcite in sea water and the effect of major physical chemical variables on the solubility has been done by Garrels and Dreyer (1952), Miller (1952), Revelle (1944), Sverdrup and others (1942), Smith (1940), Wattenberg (1936), Wattenberg and Timmerman (1936), and Trask (1936). Calculated solubility products in sea water, although not in close agreement, are all about  $10^{-6}$ —a value of sufficient precision for comparison with dolomite and apatite determinations. The solubility of calcium carbonate in sea water is affected in the following ways:

1. Solubility increases with increase in total pressure on the system.
2. Solubility increases with increase in total amount of  $\text{CO}_2$ ; as Garrels and Dreyer (1952) point out, however, the increase is due to the decrease in pH—at constant pH the solubility decreases with an increase in the  $\text{CO}_2$  concentration.
3. Solubility decreases with an increase in salinity owing to loss of  $\text{CO}_2$ , though an increase in salinity (ionic strength), particularly by the addition of ions other than  $\text{Ca}^{+2}$  and  $\text{CO}_3^{-2}$ , generally results in increased solubility.
4. Solubility decreases with increase in temperature.
5. Solubility decreases with increase in pH.

The variables important in determining  $\text{CaCO}_3$  equilibrium are, in part at least, not entirely independent, particularly the relation between pH and  $\text{CO}_2$  concentration, as the latter is the principal control of pH in sea water. In solution,  $\text{CO}_2$  forms the radicals  $\text{HCO}_3^{-1}$  and

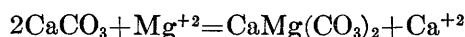
$\text{CO}_3^{-2}$ . These in conjunction with those of boron and phosphorus make up what is called the alkalinity or "excess base" of sea water and give sea water a large buffer capacity (Moberg and others, 1934) that tends to limit pH to a small range.

Most solubility-product determinations indicate that sea water, in general, is saturated or nearly saturated with calcium carbonate; and considering the factors that affect the solubility, supersaturation and conditions favorable for precipitation generally occur in near-surface waters that are relatively of high temperature, low pressure, and low  $\text{CO}_2$  concentration.

#### SOLUBILITY OF DOLOMITE

The solubility of dolomite has not been studied as extensively as that of calcite, and much of what is known is due to the work of Mitchell (1923), Klähn (1928), Bär (1932), Halla (1935), Yanat'eva (1949, 1950, 1954, and 1956), Yanat'eva and Danilova (1956), and Sveshnikova (1952). An excellent review of the dolomite system has been made by Faust (1949) and Faust and Callaghan (1948).

Halla (1935) has determined the solubility product of dolomite at  $25^\circ\text{C}$  under a partial  $\text{CO}_2$  pressure of about 1 atm (atmosphere); and he has calculated the thermodynamic equilibrium of the following reaction:



$$F = -1150 \pm 50 \text{ cal at } 25^\circ\text{C in sea water}$$

with

$$\frac{\text{Ca}^{+2}}{\text{Mg}^{+2}} = 0.197$$

The attainment of equilibrium can be questioned because Halla did not experimentally determine the reversibility of the reaction. If only the sign of the free-energy value ( $F$ ) for the above reaction in sea water is correct, however, it indicates that dolomite is the solid phase in equilibrium with the solution from which it formed and for which the system is at its lowest energy state. Halla shows that the principal factor in determining the equilibrium of the reaction is the ratio of the concentrations  $\text{Ca}^{+2}/\text{Mg}^{+2}$  in solution. The value of the solubility product for dolomite determined by Halla is  $3 \times 10^{-17}$  at  $25^\circ\text{C}$ . An approximate check of this solubility product is provided by the data of Klähn. The average solubility of three virtually pure samples of dolomite in water free of  $\text{CO}_2$  at  $15\text{--}20^\circ\text{C}$  is 0.023 g per 1000 cc of solution (Klähn, 1928, p. 537), and the solubility product calculated from that value is  $8 \times 10^{-16}$ . Klähn did not achieve complete equilibrium in his determinations, but the error involved is probably not

great. Even so, a greater solubility of dolomite would increase the difference between the values of Halla and Klähn, and thus these values give only magnitude of the dolomite solubility product.

Klähn (1928) found that dolomite is less soluble than calcite in water free of  $\text{CO}_2$  at 15–20°C. Dolomite is also less soluble than calcite in solutions at 25°C under a  $\text{CO}_2$  pressure of 1 atm (Yanat'eva, 1949 and 1954; and Sveshnikova, 1952). At a  $\text{CO}_2$  pressure of 0.0012 atm, however, Yanat'eva (1954) found that dolomite is more soluble than calcite. This indicates, according to Yanat'eva, that dolomite is incongruently soluble (the elements or radical in solution are in different proportion than they are in the solid compound) at low  $\text{CO}_2$  pressures, and it supports Bar's (1932) earlier hypothesis of a congruent-incongruent solubility dependent on  $\text{CO}_2$  concentration. Halla (1936) contends that this is an impossible relationship on the basis of the nature of equilibrium constants and that only temperature could produce a change from one condition to the other. However, Yanat'eva (1956) did find that dolomite is incongruently soluble above 65°–66°C at 1 atm of  $\text{CO}_2$  pressure and that calcite is the stable phase in saturated solutions of a 1:1 calcium-magnesium mole ratio. This problem is of particular importance in diagenetic and metamorphic reactions and more determinations are needed in the experimentally difficult low  $\text{CO}_2$  pressure range to clarify it. The argument is not critical, however, to the considerations here of primary relationships.

The solubility of dolomite is affected by other variables in the same way as that of calcite. Between 0° and 70°C and at 1 atm of  $\text{CO}_2$  pressure, the solubility of dolomite increases with a decrease in temperature (Yanat'eva, 1956), and the solubility increases with an increase of the concentration of NaCl solution up to 2 percent (Yanat'eva, 1949).

If dolomite is the stable phase in average sea water with respect to calcite over the range of sea-water temperatures, as the data of Halla (1935) and Yanat'eva (1956) indicate, a calcite precipitate would be expected to change to dolomite with time, as long as it remained in contact with sea water. Such a process is generally called penecontemporaneous dolomitization, in which the amount of dolomitization is directly related to the length of time that the calcite is in contact with sea water, and the time factor is related to the rate of sedimentation and subsidence. This type of dolomitization has been suggested by Fause and Callaghan (1948, p. 60, 63).

#### SOLUBILITY OF CARBONATE-FLUORAPATITE

The solubility of carbonate-fluorapatite in any type of solution has not been determined except by Graham (1925, p. 324) who measured the solubility of the phosphate rock of the Phosphoria formation and

other naturally occurring phosphate rock mixed with limestone in various salt and acid solutions, presumably at room temperature. Some early work on the solubility of calcium phosphate in water and in salt solution was done by Cameron and Siedel (1904), Cameron and Hurst (1904), and Sendroy and Hastings (1927). Rivière (1941) determined the solubility of calcium phosphate in sea water at several pH's and concentrations of  $\text{CO}_2$ . Dietz, Emery, and Shepard (1942) used the data of Sendroy and Hastings to calculate a solubility product of  $3.73 \times 10^{-25}$  for  $\text{Ca}_3(\text{PO}_4)_2$  in sea water at  $38^\circ\text{C}$  and concluded that sea water is nearly saturated with phosphate. Since carbonate-fluorapatite is presumably the stable phosphate compound in sea water, its solubility product would be even less than the one calculated for tricalcium phosphate.

Important work with regard to the relationship of phosphate in sea water has been done by Kazakov (1937, 1938, and 1950) and Kazakov and Sokolova (1950). Kazakov studied the system  $\text{CaO-P}_2\text{O}_5\text{-HF-H}_2\text{O}$  at the  $25^\circ\text{C}$  isotherm over a range of low concentrations to determine the solid phases formed and the regions in which they are stable. The liquid phase in equilibrium with fluorapatite at a pH of about 8 was determined to contain 0.100 mg per l of  $\text{P}_2\text{O}_5$  and 1.0–10.0 mg per l of fluorine, Kazakov holds these values to be similar to those in ocean water of the upper and middle part of the shelf. The CaO content of the liquid phase, however, is disturbingly far below that of average sea water. In this system, it is noteworthy that Kazakov found fluorapatite, to be the only stable phosphate mineral in the range of compositions that approximate those found in sea water. The phosphate mineral of the Meade Peak member is carbonate-fluorapatite, but Kazakov found only fluorapatite in his experiments because  $\text{CO}_2$  is not a component of the system; he assumed that the effect of  $\text{CO}_2$  would not greatly change the conditions, except that the solid phase would be carbonate-fluorapatite. On this point Rivière (1941) found that calcium phosphate in sea water transforms to a phosphocarbonate.

Kazakov (1937 and 1938) and Krumbein and Garrels (1952, p. 9) note that the factors affecting the solubility of  $\text{CaCO}_3$  also affect the solubility of the phosphate mineral in the same way. Thus it appears that a change in conditions that would favor the precipitation of carbonate minerals would also favor the precipitation of carbonate-fluorapatite, although they need not precipitate together.

#### EXPLANATION OF PHASE RELATIONS

The solubility studies provide data that deal mostly with the individual relationships of calcite, dolomite, and apatite with sea water; they furnish but little information about the mutual relation-

ships of the compounds. Possible mutual relationships can be described qualitatively, however, in terms of simple phase equilibria.

The system has four components. If temperature and pressure are constant, the system may be completely described in terms of the phases that may be present at various compositions of the total system. A theoretical example of such a system illustrates some of the possible relationships. Let the four components be three compounds,  $A-B-C$ , with a common ion that do not form double compounds, and water that does not form hydrates with any of the compounds. The following states of the system or associations in the system are possible: (a) 1 phase—all solution; (b) 2 phases—1 compound plus solution; (c) 3 phases—2 compounds plus solution; and (d) 4 phases—3 compounds plus solution.

A general course of crystallization upon evaporation of an unsaturated solution could result in the sequential appearance of 1, 2, and 3 solid phases (compounds  $A$ ,  $B$ , and  $C$ ). The phase that appears first depends upon the total composition of the unsaturated solution. Two solid phases—that is,  $A+B$ ,  $B+C$ , or  $A+C$ —could form as the first precipitate, but the range of composition in the unsaturated solution for which this could occur is small in comparison to that for the formation of one solid phase. Also, if two compounds precipitate together, the ratio of their amounts is likely to change as evaporation proceeds. Three solid phases could only form at the same time from one specific composition of solution. This composition is the invariant point of the system, the conditions under which the system is completely and rigorously defined. This kind of crystallization represents a differentiation of a solution by the continual removal of water, and the stage of differentiation attained depends on the amount of water removed from the system. Another kind of crystallization occurs if one of the compounds,  $A$ , for example, is continuously added to a solution that is saturated with respect to  $A$ . Although obvious, it is important to note that  $A$  will begin and continue to precipitate as long as the addition of  $A$  is the only change imposed on the system.

These phase relations for a four-component system are the simplest possible, and it is unlikely that the mineral relationships in natural systems are as uncomplicated. The general principles, however, provide a basis for understanding the factors that may relate to the formation of common ion mineral associations.

#### PHASE RELATIONS IN THE ROCKS OF THE MEADE PEAK PHOSPHATE SHALE MEMBER

The mineral mixtures of dolomite, calcite, and carbonate-fluorapatite in the rocks of the Meade Peak member can be described in terms of phase equilibria. The mineral mixtures, shown in figure 12 and discussed previously, are considered to represent three principal

kinds of mineral association: apatite alone, dolomite-apatite, and dolomite-calcite. No true primary ternary mixtures, in terms of phase relationships, are represented or can be recognized if any exist, because of the very wide range of proportions of the minerals in the apparent ternary mixtures.

The large group of samples in which apatite occurs alone indicates that apatite was the first and only mineral to form under the conditions and for the period of time in which the beds were deposited. This could have resulted from a first-stage differentiation of sea water or by the addition of phosphate by a special means.

The only other distinct group of samples, shown in the dolomite corner of figure 12, consists essentially of dolomite-apatite mixtures, although a few samples near the dolomite-calcite boundary are better considered as mixtures of dolomite and calcite. The dolomite-apatite mixtures are interpreted to represent the stage following the single-phase precipitation of apatite in which dolomite and apatite form together. A high ratio of dolomite to apatite would be expected because sea water contains much more carbonate than phosphate. The dolomite-apatite and the apatite-alone groups together make up a majority of all the samples and represent the dominant types of mineral associations in the section. The other samples of dolomite and apatite mixtures, not included in these groups, are considered in this hypothesis as products of special processes.

Dolomite and calcite mixtures cover a wide range of proportions that is not readily explained in terms of simple phase relations, but metastable precipitation probably can account for the mineral associations. Under conditions in which dolomite is the single solid phase in equilibrium with sea water of a certain composition, calcite could precipitate metastably and change with time, while in contact with sea water, to dolomite—the stable phase. In this manner, the amount of dolomite formed is a function of the length of time that the calcite is in free contact with sea water, and thus all proportions of dolomite and calcite are possible.

### CONCLUSIONS

From the foregoing considerations, it seems likely that the mineral mixtures of dolomite, calcite, and carbonate-fluorapatite in the rocks of the Meade Peak member can be explained, in part, by phase relationships. Although the interpretations are largely speculative because of the lack of critical criteria for evaluating the effect of many factors within and outside the system, three principal modes of formation of the three minerals from sea water are postulated:

1. Precipitation by an increase in total salinity, owing to evaporation.

Starting with a moving mass of sea water near the saturation



point with respect to one or more of the three solid phases—dolomite, calcite, and carbonate-fluorapatite—at a constant temperature and pressure, precipitation of one or more phases will occur upon evaporation of water and consequent increase in concentration of the three compounds. With continuing loss of water, the course of precipitation would be like that described previously in the explanation of the phase relationships—probably one solid phase first, then two, and conceivably all three solid phases if the differentiation proceeds sufficiently far. This method of precipitation is likely if a mass of sea water moves into an environment in which loss of water by evaporation is the principal change in the system. If the solid phases formed from this moving mass of sea water are deposited directly under the area in which they were precipitated, the deposits would show an ideal lateral compositional gradation in the direction of the movement of the water from only one mineral to mixtures of two minerals in changing proportions to a final deposit of three minerals in fixed proportion (fig. 13).

Scruton (1953) has described this kind of precipitation in terms of a salinity gradient that can be established in inland seas and that can produce lateral facies of limestone, anhydrite, and salt.

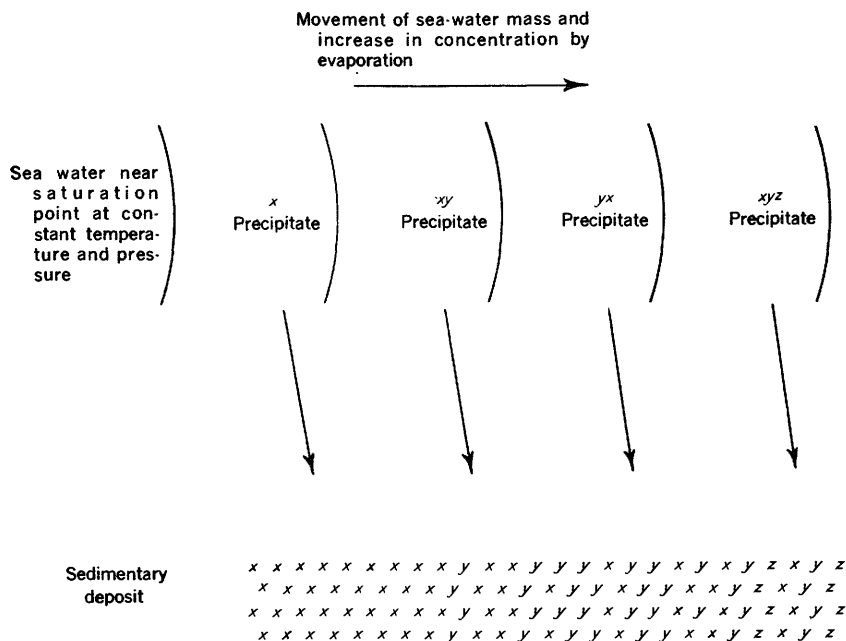


FIGURE 13.—Diagram showing formation and deposition of dolomite, carbonate-fluorapatite, and calcite from a moving mass of sea water by a decrease in the amount of total solution owing to evaporation and a consequent increase in total salinity.

Lang (1937, p. 885) and Richter-Bernburg (1955) have also used the concept of the salinity gradient as an explanation of evaporite facies in the Permian of New Mexico and Texas and in the Zechstein and other evaporites of Germany, respectively.

2. Precipitation by a relative increase in the concentration of one component. Again assuming a constant temperature and pressure for a mass of sea water that is near the saturation point with respect to one or more of the three solid phases and that is moving into an environment in which the relative concentration of one component is increased by addition of the component to the system from a previously unavailable source, precipitation of the added component will occur. The increase in concentration of one component can be produced by the release to solution of the component from organisms or by mixing with other sea water that contains a higher concentration of the component. In this mode of precipitation only the solid phase of the component will form and continue to form as long as the conditions defined above prevail. Figure 14 illustrates this concept. Organisms, particularly phytoplankton, are a probable cause of this type of formation by returning to solution upon their death and consequent decomposition the constituents they extracted by their life process. For example, the rapid dissolution of phosphorus from organisms upon their death is well established (Sverdrup and others, 1942, p. 260); and if this occurred in bottom water already saturated with apatite, the released phosphorus would precipitate immediately as apatite.
3. Precipitation by a change in temperature and pressure. In the phase relationships previously described these two variables have been considered to be constant for the purpose of simplification. Aside from their direct effect upon the kind of mineral structure that can form, temperature and pressure affect the composition of sea water by helping to control the  $\text{CO}_2$  equilibrium which, in turn, plays a large part in determining the pH of sea water. As mentioned previously the effect of changes in temperature and pressure upon the solubility of the three minerals is qualitatively the same—increasing temperature and decreasing pressure decrease the solubility of the minerals. On that basis and to the extent that temperature and pressure effects can be treated independently of concentration, the course of precipitation as a result of increasing temperature and decreasing pressure would be similar to type 1 above, but the effects would be small by comparison and more by way of modification than control.

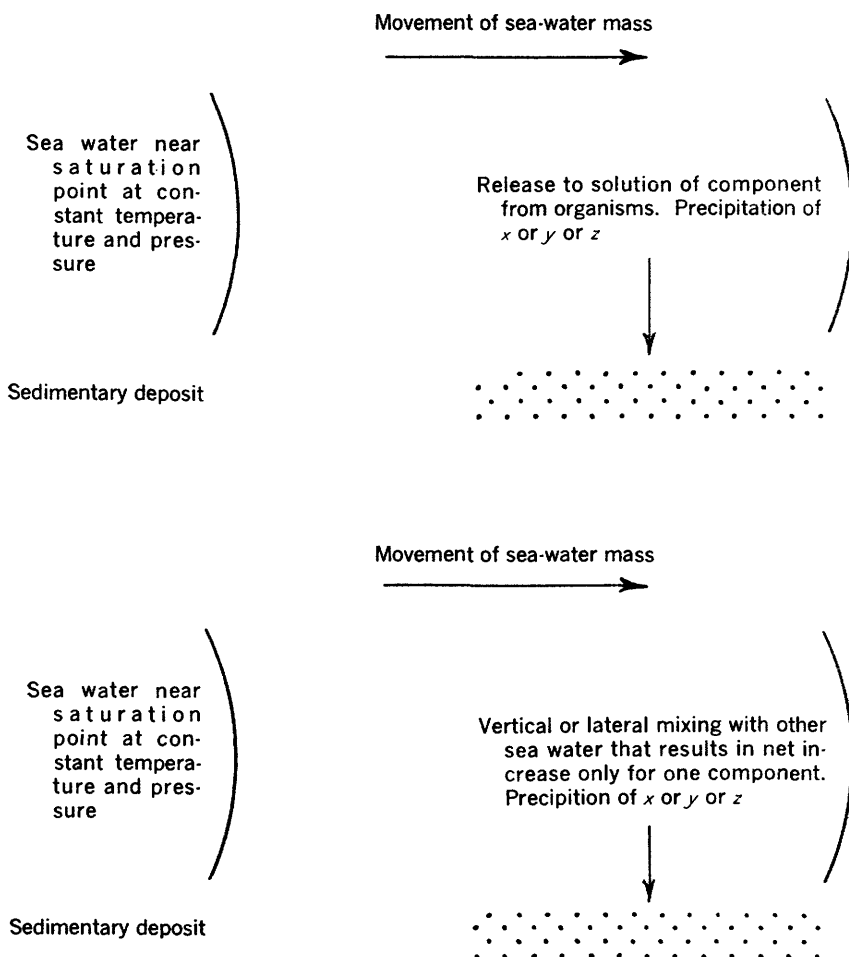


FIGURE 14.—Diagram showing formation and deposition of dolomite or carbonate-fluorapatite or calcite by a relative increase in the concentration of one component in a moving mass of sea water.

The relation of modes of formation 1 and 3 to rock facies is plain. If the locus of differentiation in a current of sea water remains stationary for a considerable period of time, continuous deposits will form which are grossly different in composition from one place to another. The different compositions will constitute distinct facies of the depositional unit. However, the locus of differentiation cannot be expected to remain stationary; more likely it will shift around, though favoring one position on a frequency basis. A shifting locus of differentiation would mean shifting facies, so a vertical section at any one place would represent a recapitulation of lateral facies changes. Thus the phosphorites and carbonate rocks of the Coal

Canyon section may represent various lateral facies. Rocks composed mostly of apatite and rocks of dolomite-apatite mixtures are the most abundant types, and it is suggested that the latter may be lateral facies of some phosphorites. A possible example of this kind is illustrated by the compositional change in the well-defined lower phosphate zone between the southeastern Idaho area and Coal Canyon. The lower phosphate zone in southeastern Idaho is about 6 feet thick and is one of the principal high-grade zones of economic value in the Meade Peak member. It is composed largely of carbonate-fluorapatite, a small amount of quartz and silicate minerals, and only a trace of carbonate minerals. At Coal Canyon this interval, beds P-8 through P-15, contains about the same relative amount of quartz and silicate minerals, but dolomite occurs in large amounts at the expense of carbonate-fluorapatite.

Sharp contacts between beds and marked changes in the proportion of the minerals, as described previously, are understandable on the basis of the principles presented; for example, the change from precipitation of apatite alone to a dolomite-apatite mixture is sharp and the proportion of dolomite to apatite is high.

Mode of formation 2 is an appealing explanation of the origin of phosphorites when some other factors are considered. The phosphorites are dark brownish gray to black and contain an appreciable amount of carbonaceous material. This suggests, along with the fine-grain size of associated detrital material, that the rocks were formed in a low part of the Phosphoria sea basin where circulation was poor and the water deficient or low in oxygen. Sea water in a low part of the basin would also have been more saline and, therefore, more dense than that in higher parts, if a significant range of salinity was produced in the Phosphoria sea water by evaporation. Such bottom water would certainly be saturated with respect to apatite if it is assumed that normal sea water is nearly so. Under these conditions, as previously mentioned, the addition of phosphorus to the system by the decomposition of dead organisms would precipitate as apatite. Apatite formed in this manner would likely not be a first precipitate but would follow one or both of the carbonate minerals.

The formation of apatite in this manner can be explained as well, however, in surface waters as those on the bottom. If a salinity gradient exists in the surface water, a saturation point is reached whereby any phosphate released by dead organisms (whose death could have been due to increased salinity) must be precipitated. Under these conditions apatite would be a first rather than a late precipitate, and sea water differentiation could even continue as in the case of evaporation.

## REFERENCES CITED

- Ahrens, L. H., 1952, The use of ionization potentials: *Geochim. et Cosmochim. Acta*, v. 2, p. 155-169.
- Altschuler, Z. S., Cisney, E. A., and Barlow, I. H., 1952, X-ray evidence of the nature of carbonate-apatite [abs.]: *Am. Mineralogist*, v. 63, p. 1230-1231.
- Altschuler, Z. S., Clarke, R. S., Jr., and Young, E. J., 1954, Uranium in apatite: *Geol. Soc. America Bull.*, v. 65, p. 1225-1226.
- Andrews, K. W., 1950, An X-ray examination of a sample of pure calcite and of solid-solution effects in some natural calcites: *Mineralog. Mag.*, v. 29, p. 85-99.
- Bär, Otto, 1932, Beitrag zum Thema Dolomitentstehung: *Centralbl. Mineralogie, Geologie, Paleontologie*, A, p. 46-62.
- Baskin, Yehuda, 1956, A study of authigenic feldspars: *Jour. Geology*, v. 64, p. 132-155.
- Bennett, C. A., and Franklin, N. L., 1954, Statistical analysis in chemistry and the chemical industry: New York, John Wiley and Sons.
- Bentor, Y. K., 1953, Relations entre la tectonique et les depots de phosphates dans le Neguev israelien: *Internat. Geol. Cong., 19th, Algiers 1952, Comptes rendus*, sec. 11, pt. 11, p. 93-102.
- Blackwelder, Eliot, 1915, Origin of the Rocky Mountain phosphate deposits: *Geol. Soc. America Bull.*, v. 26, p. 100-101.
- Bowen, N. L., and Tuttle, O. F., 1950, The system  $m\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-H}_2\text{O}$ : *Jour. Geology*, v. 58, p. 489-511.
- Brongersma-Sanders, M., 1948, The importance of upwelling water to vertebrate paleontology and oil geology: *K. Akad. Wetensch. Amsterdam Verh.*, 2d sec. 1, pt. 45, no. 4.
- Brooks, R., Clark, L. N., and Thurston, E. F., 1950, Calcium carbonate and its hydrates: *Royal Soc. London Philos. Trans.*, v. 243, p. 145-167.
- Cameron, F. K., and Hurst, L. A., 1904, Action of water and saline solutions upon certain slightly soluble phosphates: *Am. Chem. Soc. Jour.*, v. 26, p. 855.
- Cameron, F. K., and Siedel, A., 1904, Action of water on phosphates of calcium: *Am. Chem. Soc. Jour.*, v. 26, p. 14-54.
- Chave, K. E., 1952, A solid solution between calcite and dolomite: *Jour. Geology*, v. 60, p. 190-192.
- 1954a, Calcareous marine organisms, pt. 1 of Aspects of the biogeochemistry of magnesium: *Jour. Geology*, v. 62, p. 266-283.
- 1954b, Calcareous sediments and rocks, pt. 2 of Aspects of the biogeochemistry of magnesium: *Jour. Geology*, v. 62, p. 587-599.
- Chilingar, G. V., 1956, Relationship between Ca/Mg ratio and geologic age: *Am. Assoc. Petroleum Geologists Bull.*, v. 40, p. 2256-2266.
- Clarke, F. W., 1924, The data of geochemistry: *U.S. Geol. Survey Bull.* 770.
- Clarke, F. W., and Wheeler, W. C., 1922, The inorganic constituents of marine invertebrates: *U.S. Geol. Survey Prof. Paper* 124.
- Coleman, R. G., and Delevaux, Maryse, 1957, Occurrence of selenium in sulfides from some sedimentary rocks of the western United States: *Econ. Geology*, v. 52, p. 499-527.
- Cressman, E. R., 1955, Physical stratigraphy of the Phosphoria formation in part of southwestern Montana: *U.S. Geol. Survey Bull.* 1027-A, p. 1-31.
- Dietz, R. S., Emery, K. O., and Shepard, F. P., 1942, Phosphorite deposits on the sea floor of southern California: *Geol. Soc. America Bull.*, v. 53, p. 815-848.
- Emery, K. O., 1956, Sediments and water of Persian Gulf: *Am. Assoc. Petroleum Geologists Bull.*, v. 40, p. 2354-2383.

- Emery, K. O., and Rittenberg, S.C., 1952, Early diagenesis of California Basin sediments in relation to origin of oil: *Am. Assoc. Petroleum Geologists Bull.*, v. 36, p. 735-806.
- Emigh, G. D., 1958, Petrography, mineralogy, and origin of phosphate pellets in western Permian formations and other sedimentary formations: *Idaho Bur. of Mines and Geology, Pamph.* 114, 60 p.
- Evans, R. C., 1948, *Crystal chemistry*: Cambridge, University Press.
- Faivre, R., 1944, Studies, by X-ray diffraction and dilatometric analysis, of mixed carbonates of calcium and strontium and their transformations: *Acad. Sci. [Paris] Comptes rendus*, v. 219, p. 73-74.
- Faivre, R., and Chaudron, G., 1948, Relation between the structure and the physicochemical character of stability in mix crystals of the alkaline earth carbonates: *Acad. Sci. [Paris] Comptes rendus*, v. 226, p. 903-905.
- Faust, G. T., 1949, Dedolomitization, and its relation to a possible derivation of a magnesium-rich hydrothermal solution: *Am. Mineralogist*, v. 34, p. 789-823.
- Faust, G. T., and Callaghan, Eugene, 1948, Mineralogy and petrology of the Currant Creek magnesite deposits and associated rocks of Nevada: *Geol. Soc. America Bull.*, v. 59, p. 11-74.
- Ferrari, A., and Colla, C., 1936, Solid solutions between neutral rhombohedral carbonates of bivalent metals: *Gazz. chim. italiana*, v. 66, p. 571-580.
- Folk, R. L., and Weaver, C. E., 1952, A study of the texture and composition of chert: *Am. Jour. Sci.*, v. 250, p. 498-510.
- Fron del, Clifford, and Bauer, L. H., 1955, Kutnahorite; a manganese dolomite,  $\text{CaMn}(\text{CO}_3)_2$ : *Am. Mineralogist*, v. 40, p. 748-760.
- Garrels, R. M., and Dreyer, R. M., 1952, Mechanism of limestone replacement at low temperatures and pressures: *Geol. Soc. America Bull.*, v. 63, p. 325-379.
- Goddard, E. N., chm., and others, 1948, Rock-color chart: Washington, D.C., Natl. Research Council; reprinted by *Geol. Soc. America*, 1951.
- Goldsmith, J. R., and Graf, D. L., 1957, The system  $\text{CaO-MnO-CO}_2$ : Solid-solution and decomposition relations: *Geochim. et Cosmochim. Acta*, v. 11, p. 310-334.
- Goldsmith, J. R., Graf, D. L., and Joensu, O. I., 1955, The occurrence of magnesian calcites in nature: *Geochim. et Cosmochim. Acta*, v. 7, p. 212-230.
- Goodyear, J., and Duffin, W. J., 1954, The identification and determination of plagioclase feldspars by the X-ray powder method: *Mineralog. Mag.*, v. 30, p. 306-326.
- Graf, D. L., and Goldsmith, J. R., 1955, Dolomite-magnesian calcite relations at elevated temperatures and  $\text{CO}_2$  pressures: *Geochim. et Cosmochim. Acta*, v. 7, p. 109-128.
- Graf, D. L., and Lamar, J. E., 1955, Properties of calcium and magnesium carbonates and their bearing on some uses of carbonate rocks, in *Pt. 2 of Economic Geology*, 50th anniversary volume, 1905-55: Urbana, Ill., Econ. Geology Pub. Co., p. 639-713.
- Graham, W. A. P., 1925, Experiments on the origin of phosphate deposits: *Econ. Geology*, v. 20, p. 319-334.
- Gruner, J. W., and McConnell, D., 1937, The problem of the carbonate-apatites: *Zeitschr. Kristallographie, Abt. A*, v. 97, p. 208-215.
- Halla, Franz, 1935, Eine Method zur Bestimmung der Änderung freien Energie bei Reaktionen des Typus  $\text{A(s)} + \text{B(s)} = \text{AB(s)}$  and ihre Anwendung auf das Dolomitproblem: *Zeitschr. phys. Chemie, Abt. A*, v. 175, p. 63-82.
- 1936, Bemerkungen zur kongruenten Löslichkeit des Dolomits: *Zeithschr. phys. Chemie, Abt. A*, v. 175, p. 396-399.

- Harker, R. I., and Tuttle, O. F., 1955, Studies in the system  $\text{CaO-MgO-CO}_2$ . Part 2. Limits of solid solution along the binary join  $\text{CaCO}_3\text{-MgCO}_3$ ; *Am. Jour. Sci.*, v. 253, p. 274-282.
- Hendricks, S. B., and Hill, W. L., 1942, The inorganic constitution of bone: *Science*, v. 97, p. 255-257.
- 1950, The nature of bone and phosphate rock: *Natl. Acad. Sci. Proc.*, v. 36, p. 731-737.
- Hendricks, S. B., Hill, W. L., Jacob, K. D., and Jefferson, M. E., 1931, Structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopical and x-ray diffraction examinations: *Indus. and Eng. Chem.*, v. 23, p. 1413-1418.
- Honess, A. P., and Jeffries, C. D., 1940, Authigenic albite from the Lowville limestone at Bellefonte, Pennsylvania: *The Pennsylvania State College Mineral Industries Expt. Sta. Tech. Paper* 53.
- Ingerson, Earl, and Ramisch, J. L., 1942, Origin of shapes of quartz sand grains: *Am. Mineralogist*, v. 27, p. 595-606.
- Jacob, K. D., Hill, W. L., Marshall, H. L., and Reynolds, D. S., 1933, The composition and distribution of phosphate rock with special reference to the United States: *U.S. Dept. Agriculture Tech. Bull.* 364, p. 1-89.
- Kazakov, A. V., 1937, The phosphorite facies and the genesis of phosphorites, in *Geological investigations of agricultural ores: Leningrad, Sci. Inst. Fertilizers and Insecto-Fungicides Trans.*, No. 142 (published for the 17th sess. *Internat. Geol. Cong.*), p. 95-113.
- 1938, The phosphorite facies and the genesis of natural phosphates: *Soviet Geol.*, v. 8, p. 33-47.
- 1950, The fluorapatite equilibrium system in the conditions of formation of sedimentary rocks: *Akad. Nauk SSSR, Inst. Geol. Nauk Trudy*, v. 114, *Geol. ser. no.* 40, p. 1-21.
- Kazakov, A. V., and Sokolova, E. I., 1950, Conditions of the formation of fluorite in sedimentary rocks: *Akad. Nauk SSSR, Inst. Geol. Nauk Trudy*, v. 114, *Geol. ser. no.* 40, p. 22-64.
- Keller, W. D., 1941, Petrography and origin of the Rex chert: *Geol. Soc. America Bull.*, v. 52, p. 1279-1297.
- Klähn, Hans, 1928, Süßwässerkalkmagnesiagesteine und Kalkmagnesiassüßwässer: *Chem. Erde*, v. 2, p. 453-587.
- Krauskopf, K. B., 1955, Sedimentary deposits of rare metals; in *Pt. 1 of Economic Geology, 50th anniversary volume, 1905-55: Urbana, Ill., Econ. Geology Pub. Co.*, p. 411-463.
- 1956, Factors controlling the concentrations of thirteen rare metals in sea-water: *Geochim. et Cosmochem. Acta*, v. 9, p. 1-32.
- Krieger, Philip, 1930, Notes on an X-ray diffraction study of the series calcite-rhodochrosite: *Am. Mineralogist*, v. 15, p. 23-29.
- Krumbein, W. C., and Garrels, R. M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: *Jour. Geology*, v. 60, p. 1-33.
- Kulp, J. L., Turekian, K. K., and Boyd, D. W., 1952, Strontium content of limestones and fossils: *Geol. Soc. America Bull.*, v. 63, p. 701-716.
- Lang, W. B., 1937, The Permian formations of the Pecos Valley of New Mexico and Texas: *Am. Assoc. Petroleum Geologists Bull.*, v. 21, p. 833-898.
- Lowell, W. R., 1952, Phosphatic rocks in the Deer Creek-Wells Canyon area, Idaho: *U.S. Geol. Survey Bull.* 982-A, p. 1-51.
- Lowenstam, H. A., 1954, Factors affecting the aragonite: calcite ratios in carbonate-secreting marine organisms: *Jour. Geology*, v. 62, p. 284-322.

- McConnell, Duncan, 1938, A structural investigation of the isomorphism of the apatite group: *Am. Mineralogist*, v. 23, p. 1-19.
- 1950, The petrography of rock phosphates: *Jour. Geology*, v. 58, p. 16-23.
- 1952, Structural substitutions involving  $\text{CO}_3$  and OH, pt. 4 of *The problem of the carbonate apatites*: *Soc. française Mineralogie et cristallographie Bull.*, v. 75, p. 428-445.
- 1953, Radioactivity of phosphatic sediments: *Econ. Geology*, v. 48, p. 147-148.
- McKelvey, V. E., 1946, Preliminary report on stratigraphy of the phosphatic shale member of the Phosphoria formation in western Wyoming, southeastern Idaho, and northern Utah: U.S. Geol. Survey open-file report, 158 p.
- McKelvey, V. E., and Carswell, L. D., 1956, Uranium in the Phosphoria formation, in Page, L. R., Stocking, H. E., and Smith, H. B. (compilers), *Contributions to the geology of uranium and thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy*, Geneva, Switzerland, 1955: U.S. Geol. Survey Prof. Paper 300, p. 483-487.
- McKelvey, V. E., Everhart, D. L., and Garrels, R. M., 1955, Origin of uranium deposits, in Pt. 1 of *Economic Geology*, 50th anniversary volume, 1905-55: Urbana, Ill., Econ. Geology Pub. Co., p. 464-533.
- McKelvey, V. E., and Nelson, J. M., 1950, Characteristics of marine uranium-bearing sedimentary rocks: *Econ. Geology*, v. 45, p. 35-53.
- McKelvey, V. E., Swanson, R. W., and Sheldon, R. P., 1953, The Permian phosphorite deposits of western United States: *Internat. Geol. Cong.*, 19th, Algiers 1952, *Comptes rendus*, sec. 11, pt. 11, p. 45-64.
- McKelvey, V. E., and others, 1953, Stratigraphic sections of the Phosphoria formation in Wyoming, 1947-48: U.S. Geol. Survey Circ. 210.
- 1956, Summary description of Phosphoria, Park City, and Shedhorn formations in western phosphate field: *Am. Assoc. Petroleum Geologists Bull.*, v. 40, no. 12, p. 2826-2863.
- MacKenzie, W. S., and Smith, J. V., 1955, Orthoclase-micropertthites, pt. 1 of *The alkali feldspars*: *Am. Mineralogist*, v. 40, p. 707-732.
- 1956, An optical and X-ray study of high temperature feldspars, pt. 3 of *The alkali feldspars*: *Am. Mineralogist*, v. 41, p. 405-427.
- Mansfield, G. R., 1927, Geography, geology and mineral resources of part of southeastern Idaho: U.S. Geol. Survey Prof. Paper 152.
- Mehmel, M., 1930, Über die Structur des Apatits I: *Zeitschr. Kristallographie*, v. 75, p. 323-331.
- 1931, Beziehungen zwischen Kristallstruktur und chemischer Formel des Apatits: *Zeitschr. phys. Chemie, Abt. B*, v. 15, p. 223-241.
- Miller, J. P., 1952, A portion of the system calcium carbonate-carbon dioxide-water, with geological implications: *Am. Jour. Sci.*, v. 250, p. 161-203.
- Mitchell, A. E., 1923, Studies on the dolomite system: *Chem. Soc. London Jour.*, v. 123, p. 1055-1065, 1087-1094.
- Moberg, E. G., Greenberg, D. M., Revelle, R. R., and Allen, E. C., 1934, The buffer mechanism of sea water: *Scripps Inst. Oceanography, Univ. California Tech. Ser.* 3, p. 231-278.
- Murray, J. W., 1954, The deposition of calcite and aragonite in caves: *Jour. Geology*, v. 62, p. 481-492.
- Náray-Szabó, St., 1930, The structure of apatite  $(\text{CaF})\text{Ca}_4(\text{PO}_4)_3$ : *Zeitschr. Kristallographie*, v. 75, p. 387-398.
- Palache, Charles, Berman, Harry, and Frondel, Clifford, 1951, *Dana's System of mineralogy*: 7th ed. New York, John Wiley and Sons.



- Posner, A. S., and Duyckaerts, G., 1954, Infared study of the carbonate in bone, teeth, and francolite: *Experimenta*, v. 10, p. 424-425.
- Ray, L. L., 1947, Quartz paramorphs after tridymite from Colorado: *Am. Mineralogist*, v. 32, p. 643-646.
- Revelle, R. R., 1944, I. Marine bottom samples collected in the Pacific Ocean by the Carnegie on its seventh cruise: *Carnegie Inst. Washington Pub.* 556.
- Richards, R. W., and Mansfield, G. R., 1912, The Bannock overthrust, a major fault in southeastern Idaho and northeastern Utah: *Jour. Geology*, v. 20, p. 681-709.
- Richter-Bernburg, G., 1955, Über salinäre Sedimentation: *Deutsche geol. Gesell. Zeitschr.*, v. 105, p. 593-645.
- Rivière, A., 1941, Sur la solubilité du phosphate tricalcique dans l'eau de mer: *Soc. géol. France Comptes rendus*, p. 50-51.
- Rogers, C. L., Cserna, Zoltan de, Tavera, Eugenio, and Ulloa, Salvador, 1956, General geology and phosphate deposits of Concepción del Oro District, Zacatecas, Mexico: *U.S. Geol. Survey Bull.* 1037-A, 102 p.
- Romo, L. A., 1954, Synthesis of carbonate-apatite: *Am. Chem. Soc. Jour.*, v. 76, p. 3924-3925.
- Rubey, W. W., 1951, Geologic history of seawater: an attempt to state the problem: *Geol. Soc. America Bull.*, v. 62, p. 1111-1148.
- Scruton, P. C., 1953, Deposition of evaporates: *Am. Assoc. Petroleum Geologists Bull.*, v. 37, p. 2498-2512.
- Sendroy, J., and Hastings, A. B., 1927, The solubility of Tertiary calcium phosphate in salt solutions and biological plants, pt. 2, and The solubility of calcium carbonate and calcium phosphate under various conditions, part 3 of *Studies of the solubility of calcium salts*: *Jour. Biol. Chemistry*, v. 71, p. 783-846.
- Sheldon, R. P., 1957, Physical stratigraphy of the Phosphoria formation in northwestern Wyoming: *U.S. Geol. Survey Bull.* 1042-E, p. 105-185.
- Silverman, S. R., Fuyat, R. K., and Weiser, J. D., 1952, Quantitative determination of calcite associated with carbonate-bearing apatites: *Am. Mineralogist*, v. 37, p. 211-222.
- Smith, C. L., 1940, Calcium carbonate precipitation, pt. 2 of *The Great Bahama Bank*: *Jour. Marine Research*, v. 3, p. 171-189.
- Smith, J. V., and MacKenzie, W. S., 1955, A simple x-ray technique for the study of alkali feldspars, pt. 2 of *The alkali feldspars*: *Am. Mineralogist*, v. 40, p. 733-747.
- Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1942, *The oceans*: New York, Prentice-Hall.
- Sveshnikova, V. N., 1952, Solubility of dolomitized limestone in  $H_2O$  at  $25^{\circ}C$ . and 1 atmosphere  $CO_2$ : *Akad. Nauk SSSR Doklady*, v. 85, p. 357-360; *Chem. Abs.*, v. 48, p. 510a.
- Thompson, M. E., 1953, Distribution of uranium in rich phosphate beds of the Phosphoria formation: *U.S. Geol. Survey Bull.* 988-D, p. 45-67.
- 1954, Further studies of the distribution of uranium in rich phosphate beds of the Phosphoria formation: *U.S. Geol. Survey Bull.* 1009-D, p. 107-123.
- Trask, P. D., 1936, Relation of salinity to the calcium carbonate content of marine sediments: *U.S. Geol. Survey Prof. Paper* 186-N, p. 273-299.
- Trautz, O. R., 1955, X-ray diffraction of biological and synthetic apatite: *New York Acad. Sci. Annals*, v. 60, p. 696-712.
- Turekian, K. K., and Kulp, J. L., 1956, The geochemistry of strontium: *Geochim. et Cosmochim. Acta*, v. 10, p. 245-296.

- Tuttle, O. F., 1952a, Optical studies on alkali feldspars (Bowen volume): *Am. Jour. Sci.*, p. 553-567.
- 1952b, Origin of the contrasting mineralogy of extrusive and plutonic salic rocks: *Jour. Geology*, v. 60, p. 107-124.
- Tuttle, O. F., and Bowen, N. L., 1950, High-temperature albite and contiguous feldspars: *Jour. Geology*, v. 58, p. 572-583.
- Tuttle, O. F., and Keith, M. L., 1954, The granite problem: Evidence from the quartz and feldspar of a Tertiary granite: *Geol. Mag.*, v. 91, p. 61-72.
- Underwood, A. L., Toribara, T. Y., and Neuman, W. F., 1955, An infrared study of the nature of bone carbonate: *Am. Chem. Soc. Jour.*, v. 77, p. 317-319.
- Visse, L., 1952, Genèse des gîtes phosphatés du sud-est Algéro-Tunisien: *Internat. Geol. Cong.*, 19th, Algiers 1952, *Regional Mon.*, ser. 1, no. 27, 58 p.
- Vol'fkovich, S. I., Grinshpan, L. B., and Shekhter, A. B., 1952, The electron-microscope study of natural phosphates: *Akad. Nauk SSSR Doklady*, v. 85, p. 137-139; *Chem. Abs.*, v. 49, p. 5062g.
- Wager, L. R., Weedon, D. S., and Vincent, E. A., 1953, A granophyre from Coire Uaigneich, Isle of Skye, containing quartz paramorphs after tridymite: *Mineralog. Mag.*, v. 30, p. 263-275.
- Wattenberg, Herman, 1936, Kohlensäure und Kalciumkarbonat im Meere: *Fortschr. Mineralogie, Kristallographie und Petrographie*, v. 20, p. 168-195.
- Wattenberg, Herman, and Timmerman, E., 1936, Über die sättigung des Seewassers an  $\text{CaCO}_3$  und die anorganogene Bildung von Kalksedimenten: *Annalen Hydrographie*, v. 64, p. 23-31.
- Wayland, R. G., 1942, Composition, specific gravity, and refractive indices of rhodochrosite: Rhodochrosite from Butte, Montana: *Am. Mineralogist*, v. 27, p. 614-628.
- Weaver, C. E., 1955, Mineralogy and petrology of the rocks near the Quadrant-Phosphoria boundary in southwest Montana: *Jour. Sedimentary Petrology*, v. 25, p. 163-192.
- Weyl, W. A., 1951, A new approach to surface chemistry and to heterogeneous catalysis: *Pennsylvania State College Mineral Industries Expt. Sta. Bull.* 57.
- Winchell, A. N., 1951, Descriptions of minerals, pt. 1 of *Optical mineralogy*: 4th ed., New York, John Wiley and Sons.
- Yanat'eva, O. K., 1949, Solubility in the system  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{CO}_2$ ,  $\text{SO}_4$ ,  $\text{H}_2\text{O}$ : *Akad. Nauk SSSR Doklady*, v. 67, p. 479-481.
- 1950, Solubility of dolomite in aqueous salt solutions; *Akad. Nauk SSSR, Sektora Fiz.-Khim. Izv.*, Anal., v. 20, p. 252-268; *Chem. Abs.*, v. 48, p. 7992c.
- 1954, Solubility of dolomite in water in the presence of carbon dioxide: *Akad. Nauk SSSR, Otdel. Khim. Nauk Izv.*, no. 6, p. 1119-1120; *Chem. Abs.*, v. 49, p. 14435f.
- 1956, The nature of the solubility of dolomite in water and in solutions of calcium sulfate under different partial pressures of  $\text{CO}_2$ : *Zhur. Neorg. Khim.*, 1, p. 1473-1478; *Chem. Abs.*, v. 51, p. 1713i.
- Yanat'eva, O. K., and Danilova, E. P., 1956, Application of the diagram of solubility of the system  $\text{CaCO}_3\text{-MgCO}_3\text{-H}_2\text{O}$  for the characterization of certain carbonate rock: *Zhur. Prikad. Khim.*, 29, p. 1152-1159; *Chem. Abs.*, v. 51, p. 8597c.
- Yoder, H. S., and Eugster, H. P., 1955, Synthetic and natural muscovites: *Geochim. et Cosmochim. Acta*, v. 8, p. 225-280.
- Zeller, E. J., and Wray, J. L., 1956, Factors influencing precipitation of calcium carbonate: *Am. Assoc. Petroleum Geologists Bull.*, v. 40, p. 140-152.

# INDEX

	Page		Page
Accessory minerals.....	114	Carbonate-fluorapatite, diadochy.....	101-104
Acknowledgments.....	74	formation.....	126-128, 134-138
Albite.....	87, 89, 106, 108, 109, 110, pl. 28	mineral norm.....	87-88
Aluminum.....	81, 94, 100	percentage, mineral composition.....	86
Analyses, chemical.....	77-79, 90, 102	phase relations.....	132-134
chemical, selenium.....	85	phosphate mineral name.....	104-105
spectrographic.....	94, pl. 29	relation to apatite.....	99-101
X-ray.....	90, 95, pl. 28	solubility.....	131-132
Ankerite.....	91, 92, 97	submicrocrystalline character.....	105
Anorthite.....	109	types.....	119
Apatite, cation coordination.....	100	Chemical composition, major constituents.....	76-81
diadochy.....	99	minor constituents.....	82-86
ionic radii.....	100	Chlorine.....	101
mineral mixtures.....	123-124	Chromium.....	82, 83, 84, 100, pl. 29
phase relations.....	132-134	Cobalt.....	82, 92, 94
<i>See also</i> Carbonate-fluorapatite.		Collophane.....	104
Aragonite.....	91	Columnar section.....	pl. 28
Arsenic.....	82, 100	Conclusions.....	134-138
Barium.....	83, 91, 94, 95, pl. 29	Copper.....	83, 84, 94, pl. 29
Beryllium.....	82, 83, pl. 29	Dahlite.....	99
Bibliography.....	139-144	Dehrnite.....	99, 104
Biotite.....	87, 109, 111, 112	Dolomite, analyses, spectrographic.....	94
Boron.....	82, 83, pl. 29	analyses, X-ray.....	95
Brachiopods.....	117	d-spacing.....	97
Cadmium.....	92	diadochy.....	91-98
Calcite, analyses, spectrographic.....	94, pl. 28	formation.....	126-128, 134-138
analyses, X-ray.....	95	mineral composition.....	pl. 28
d-spacing.....	94	mineral mixtures.....	123-124
diadochy.....	91-98	mineral norm.....	87-88
formation.....	126-128, 134-138	percentage, mineral composition.....	87
mineral mixtures.....	123-124	percentage ratio to calcite.....	89-90
mineral norm.....	87-88	phase relations.....	132-134
percentage, mineral composition.....	87	solubility.....	130-131
percentage ratio to dolomite.....	89-90	Dolomite-calcite-carbonate-fluorapatite-sea	
phase relations.....	132-134	water system.....	128-129
solubility.....	129-130		
<i>See also</i> Carbonate rock.		Ellestadite.....	99, 103, 104
Calcium.....	80, 87, 91, 92, 100, 101, 104, 123	End-member rock types, chemical composi-	
Carbon.....	92, 99, 100, 101	tion, average.....	80-81
Carbonaceous material, calculation.....	89	mixtures.....	115-116
description.....	114	<i>See also</i> Carbonate rock, Phosphorite,	
percentage, composition.....	87	Quartz-silicate rock.	
Carbonate.....	98		
Carbonate rock, chemical composition.....	80,		
81, 82, 83, 102-103		Feldspar.....	105-110, 115, 116, 121, 122
cleavage.....	119	<i>See also</i> particular type.	
formation, role of organisms.....	127-128	Fermorite.....	99
inclusions.....	118	Fluorapatite.....	99
mineral composition.....	115, pl. 28	Fluorine.....	80, 89, 98, 101, 104, 105
replacement.....	118-119	Fluorite.....	87, 89, 114, pl. 28
texture.....	117	Foraminifera.....	117, pl. 28
twinning.....	119	Fossils.....	119, 120
types.....	116-117	<i>See also</i> Brachiopods, Foraminifera, Pelecypods.	
<i>See also</i> Calcite.		Francoilite.....	99, 104

	Page		Page
Geothite.....	114	Phosphorite—Continued	
Geography.....	74	inclusions.....	120
Geologic section.....	75	mineral composition.....	115, pl. 28
Gypsum.....	114	oolite development.....	121
		pellet development.....	120-121
		texture.....	119-120
Hematite.....	87, 114	types.....	119
Hydrotroilite.....	113	Phosphorus.....	80, 81, 87, 100, 101, 103, 104, 105, 127
Hydroxyapatite.....	99	Phytoplankton.....	136
		Plagioclase.....	109, pl. 28
Illite.....	87, 89, 106, 108, 111, 113, 115, 122, pl. 28	Potassium.....	81, 100, 101
Introduction.....	72-74	Pyrite.....	87, 113, 114
Investigation, methods.....	76		
previous.....	73-74	Quartz, description.....	110-111
Ionic radii.....	91-92, 100	percentage, mineral composition.....	86-87
Iron.....	81, 91, 94, 96, 97	Quartz-silicate rock, chemical composition.....	80
Iron oxides.....	113-114	81, 82, 83, 85, 102-103	
Iron sulfides.....	113	mineral composition.....	115, 121, pl. 28
Kaolin group.....	112-113	Rare earths.....	82, 100
Kaolinite.....	87, 89, 115, pl. 28	Retort member, Phosphoria formation, litho- logic character.....	75
Kutnahorite.....	97	Rex chert member, Phosphoria formation, lithologic character.....	74-75
		Rhodochrosite.....	91, 94
Lead.....	82, 83, 84, pl. 29	Rutile.....	111
Leucocene.....	114, pl. 28	Rock types, changes.....	122-123
Lewistonite.....	99	lithologic character.....	115
Limestone, mineral composition.....	pl. 28	<i>See also</i> End-member rock types.	
Limonite.....	87		
Lithologic character.....	74, 75	Selenium.....	85-86
		Shale, chemical composition.....	81
Magnesite.....	94, 97	Siderite.....	94
Magnesium.....	81, 87, 91, 92, 94, 96, 97	Silica.....	80, 103
Manganapatite.....	99	Silicon.....	100, 101, 104, 105
Mangandolomite.....	91	Silver.....	82, 83, 103, pl. 29
Manganese.....	82, 83, 91, 94, 97, 100, pl. 29	Sodium.....	81, 94, 100, 101, 102, 103
Melnikovite.....	113	Spectrometer.....	93
Mica.....	111-112	Sphalerite.....	82, 84
<i>See also</i> particular type.		Strontium.....	82, 83, 91, 94, 95, 98, 100, 103, 104, pl. 29
Microcline.....	87, 106, 108	Sublette anticline.....	74
Microphanite, definition.....	119	Sulfur.....	84, 85, 89, 100, 101, 102, 103, 105, 114
Mineral associations, relationships.....	125-126		
Mineral composition.....	86-90	<i>t</i> test, modified.....	102, 103
Mineral-norm calculations.....	87-89	"Students".....	90, 94
Molybdenum.....	82, 83, 84, pl. 29	Titanite.....	82, 87, 89, 114, pl. 28
Montmorillonite.....	113	Titanium.....	81, 82, 83, 94, pl. 29
Muscovite.....	87, 89, 106, 111, 112, 115, 116, 121, pl. 28	Tourmaline.....	82, 87, 114, pl. 28
Nickel.....	82, 83, pl. 29	Uranium.....	86, 100, 101
Oligoclase.....	109	Vanadiferous zone, carbonaceous material.....	121
Organisms, rock formation.....	127-128	element relationships.....	84-85
Orthoclase.....	87, 89, 106, 108, 109, 110, pl. 28	gypsum.....	114
Oxygen, ionic coordination.....	100	sulfur content.....	113
		Vanadium.....	82, 83, 84, 85, 94, 100, 102, 103, pl. 29
Pelecypods.....	117		
Pelletite, definition.....	119	Wilkeite.....	99, 103, 104
Phosphoria formation, age.....	72		
<i>See also</i> particular member.		Zircon.....	82, 87, 111, 112, 114, pl. 28
Phosphorite, chemical composition.....	80,	Zirconium.....	82, 83, 94, pl. 29
81, 82, 83, 85, 102-103		Zinc.....	82, 83, 84, 92, 103, pl. 29
color.....	120		
formation, circulating sea water require- ment.....	127		
role of organisms.....	127-128		

# A Method of X-Ray Analysis for Determining the Ratio of Calcite to Dolomite in Mineral Mixtures

*By* R. A. GULBRANDSEN

CONTRIBUTIONS TO GENERAL GEOLOGY

---

G E O L O G I C A L   S U R V E Y   B U L L E T I N   1 1 1 1 - D



## CONTENTS

---

	Page
Abstract.....	147
Introduction.....	147
Design of the experiment.....	148
Preparation of the mixtures.....	149
Procedure of analysis.....	149
Statistical treatment.....	150
The analysis of variance.....	150
Correlation coefficient and least-squares trend.....	151
Application.....	152
Literature cited.....	152

---

## ILLUSTRATIONS

---

FIGURE 15. Peak-height ratios of calcite to dolomite.....	151
---	-----

---

## TABLES

---

TABLE 1. A $4 \times 4$ factorial plot showing composition of 16 prepared mineral mixtures.....	148
2. Background mixtures classified according to mineral proportions.....	149
3. Mineral composition of prepared mixtures.....	149
4. Measured peak heights and ratios of calcite and dolomite in prepared mineral mixtures.....	150
5. Analysis of variance of peak-height ratios for calcite and dolomite.....	152





## CONTRIBUTIONS TO GENERAL GEOLOGY

---

### A METHOD OF X-RAY ANALYSIS FOR DETERMINING THE RATIO OF CALCITE TO DOLOMITE IN MINERAL MIXTURES

---

By R. A. GULBRANDSEN

---

#### ABSTRACT

The use of X-ray methods for determining the proportion of calcite to dolomite in carbonate rocks is apparently not common. Accordingly, an experiment was designed to test the usefulness of X-ray diffraction intensities (peak heights) of calcite and dolomite as a means of estimating the percentage ratio of these minerals in carbonate rocks of the Meade Peak phosphatic shale member of Coal Canyon, Wyo.

X-ray analyses were made of 16 prepared mineral mixtures of a known composition that was similar to that of the carbonate rocks of the phosphatic shale member. The analyses indicate that the differences between the peak heights of calcite and dolomite are due to differences in amounts of calcite and dolomite, and that the ratios of the peak heights are useful as a measure of the ratios of calcite to dolomite.

#### INTRODUCTION

The need of a method for readily determining the proportion of calcite to dolomite in rocks is well known. Differentiation by optical means in thin section is often not possible. Staining methods are not in general use because their success largely depends on characteristics of the rock other than carbonate content. The use of X-ray methods for determining the proportion of calcite to dolomite in carbonate rocks is apparently not common, and a method of measurement has been described only recently (Tennant and Berger, 1957) since this work was done. However, Stolkowski (1948), Faivre (1944), and DeKeyser and Degueldre (1950) have mentioned the quantitative use of relative diffraction intensities to measure the proportions of carbonate compounds in prepared mixtures.

The method described here has been designed and tested for a particular series of closely related rock types. Its general application is not known; however, the procedure for testing the significance of the method is applicable to other rock suites.

The statistical design of the experiment was suggested by K. R. Bennet, J. C. Griffiths, and M. A. Rosenfeld of Pennsylvania State

University. The assistance given by Mr. Rosenfeld in the statistical analysis is appreciated.

### DESIGN OF THE EXPERIMENT

An experiment was designed to test the usefulness of relative X-ray diffraction intensities of calcite and dolomite as a means of estimating their percentage ratios in carbonate rocks of the Meade Peak phosphatic shale member of Coal Canyon, Wyo. To do this, 16 mineral mixtures whose composition was similar to that of the carbonate rocks of the phosphatic shale member were prepared. The study of the composition of the mixtures was divided into: carbonate mineral composition and background mineral composition. Calcite and dolomite were each used at 4 levels of concentration—5, 20, 35, and 50 percent—providing a convenient  $4 \times 4$  factorial plot (table 1). The background mixtures included eight types composed of varying proportions of quartz, apatite, muscovite, potassium feldspar, and sodium feldspar (table 2). As an example, type IIB background mixture is composed of 10 percent muscovite, potassium feldspar, and sodium feldspar in the proportion 50:25:25; and of 90 percent quartz and apatite in the proportion 35:65. These background mixtures were each assigned twice and at random to the 16 mixtures of calcite and dolomite to determine if they had any effect upon the peak intensities of calcite and dolomite; that is, if there was any interaction. The composition of each mixture is shown in table 3.

TABLE 1.—A  $4 \times 4$  factorial plot showing composition, in percent by weight, of 16 prepared mineral mixtures

[C, percent calcite plus percent dolomite; IA-IID, percent background mixture]

Dolomite, in percent	5	1 C=10 IIB=90	2 C=25 IIC=75	3 C=40 IIC=60	4 C=55 IIB=45
	20	5 C=25 IID=75	6 C=40 IC=60	7 C=55 IC=45	8 C=70 IA=30
	35	9 C=40 IIA=60	10 C=55 ID=45	11 C=70 IID=30	12 C=85 IIA=15
	50	13 C=55 IB=45	14 C=70 IA=30	15 C=85 ID=15	16 C=100
		5	20	35	50
		Calcite, in percent			

TABLE 2.—*Background mixtures classified according to mineral proportions, in percent by weight*

[q, quartz; a, apatite; m, muscovite; k, potassium-feldspar; n, sodium-feldspar]

Type	95				5			Type	90				10		
	90	65	35	10	50	25	25		90	65	35	10	50	25	25
IA-----	a			q	m	k	n	IIA-----	a			q	m	k	n
B-----	a	a	q		m	k	n	B-----		a	q		m	k	n
C-----		q			m	k	n	C-----		q	a		m	k	n
D-----	q			a	m	k	n	D-----	q			a	m	k	n

TABLE 3.—*Mineral composition, in percent by weight, of prepared mixtures*

Sample	Calcite	Dolomite	Quartz	Apatite	Muscovite	Feldspar
1-----	5	5	28.4	52.6	4.5	4.5
2-----	20	5	43.9	23.6	3.75	3.75
3-----	35	5	35.1	18.9	3.0	3.0
4-----	50	5	14.2	26.3	2.25	2.25
5-----	5	20	60.9	6.6	3.75	3.75
6-----	20	20	37.0	20.0	1.5	1.5
7-----	35	20	27.8	15.0	1.1	1.1
8-----	50	20	2.9	25.6	.75	.75
9-----	5	35	5.4	48.6	3.0	3.0
10-----	20	35	38.6	4.2	1.1	1.1
11-----	35	35	24.3	2.7	1.5	1.5
12-----	50	35	1.4	12.1	.75	.75
13-----	5	50	15.0	27.8	1.1	1.1
14-----	20	50	2.9	25.6	.75	.75
15-----	35	50	12.8	1.4	.4	.4
16-----	50	50	0	0	0	0

The 4×4 factorial type statistical design can be used to test the following questions:

1. Are the differences between the ratios of peak heights of calcite and dolomite due to the difference in amounts of calcite and dolomite?
2. Are the peak-height ratios useful as a measure of the ratio of calcite to dolomite?

#### PREPARATION OF THE MIXTURES

The minerals were ground to pass through a 325-mesh sieve. Each mineral assigned to the mixtures was weighed on an analytical balance to within an accuracy of three decimal places. A volume of water approximately twice that of the mixtures was added, and these combinations were mechanically shaken for 2 hours. Samples were prepared for X-ray analysis by mounting the watered mixtures on glass slides with an eye dropper and rapidly drying them in an oven at 80° C.

#### PROCEDURE OF ANALYSIS

Samples were run on the Norelco X-ray spectrometer, using copper radiation. The peaks selected for measurement represented diffrac-

tion from comparable planes of calcite and dolomite and were at approximately  $29.4^\circ$  and  $30.9^\circ$   $2\theta$ , respectively. These peaks were selected because they are the peaks of greatest intensity for both calcite and dolomite, they are relatively free of interference from peaks of other minerals in the mixtures, and they are close together. The peaks were measured in recorder-chart units (4 lines per inch) from a baseline determined primarily by the background line between  $14^\circ$  and  $20^\circ$ . This part of the traverse is relatively free of peaks and provides the best indication of the background trend. The total traverse was from  $4^\circ$  to  $38^\circ$ .

Control of the X-ray procedure was kept at a minimum. The spectrometer was warmed up and the width of the slit openings was kept constant. The amplitude and damping were varied and samples were run at random (according to a table of random numbers) in groups on different days and at different times of the day. Peak-height measurements, peak-height ratios, and percentage ratios for the mixtures are shown in table 4.

TABLE 4.—*Measured peak heights and ratios of calcite and dolomite in prepared mineral mixtures*

Sample	Peak height <sup>1</sup>		Log of peak-height ratio <sup>2</sup>	Log of percentage ratio <sup>2</sup>
	Calcite	Dolomite		
1.....	0. 95	1. 05	1. 9566	2. 0000
2.....	3. 75	1. 25	2. 4771	2. 6021
3.....	4. 60	1. 05	2. 6415	2. 8451
4.....	7. 10	. 90	2. 8971	3. 0000
5.....	1. 60	4. 25	1. 5752	1. 3979
6.....	2. 70	2. 65	2. 0086	2. 0000
7.....	2. 20	4. 25	1. 7143	2. 2430
8.....	6. 80	3. 60	2. 2068	2. 3979
9.....	. 60	4. 15	1. 1614	1. 1553
10.....	3. 85	5. 35	1. 8561	1. 7566
11.....	4. 50	4. 70	1. 9809	2. 0000
12.....	7. 60	4. 80	2. 1987	2. 1553
13.....	. 95	5. 15	1. 2648	1. 0000
14.....	3. 45	7. 70	1. 6513	1. 6021
15.....	4. 50	5. 30	1. 9289	1. 8451
16.....	5. 15	5. 30	1. 9877	2. 0000

<sup>1</sup> Measurements in recorder-chart units.

<sup>2</sup> Logarithm of 100 times the ratio.

### STATISTICAL TREATMENT

*The analysis of variance.*—The statistical method used is the analysis of variance—an extremely useful method whose applicability to geological problems has been well illustrated by Krumbein and Miller (1953). Logarithms of the ratios were used so that a plot of the peak-height ratios against the percentages would be a linear function. The plot of the logarithms of these values on arithmetic

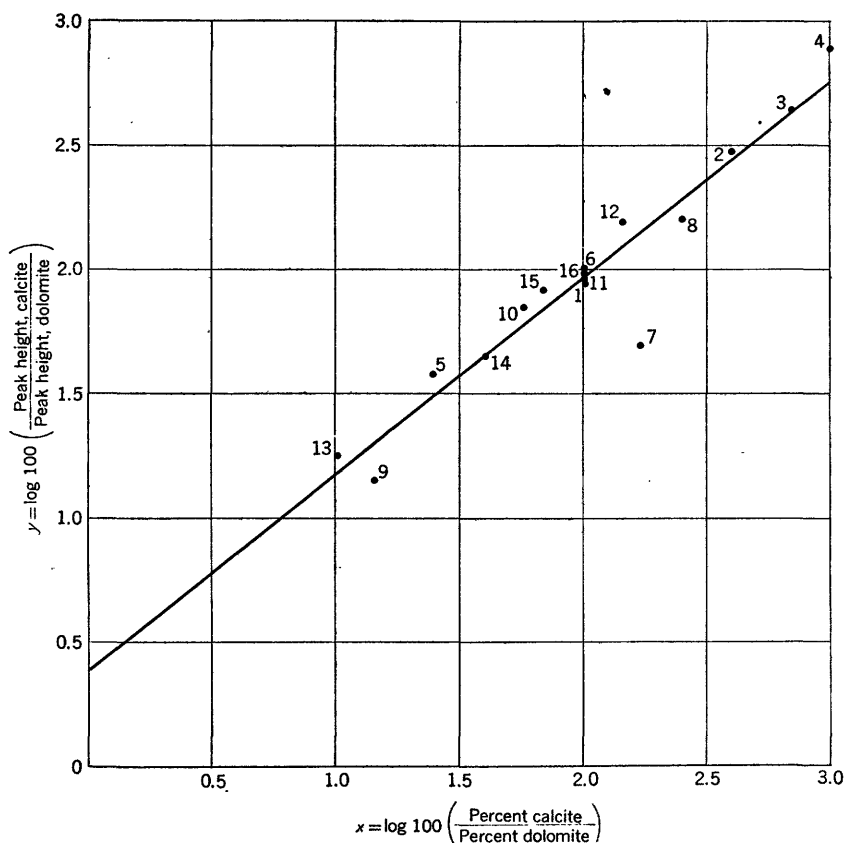


FIGURE 15.—Peak-height ratios of calcite to dolomite plotted against percentage ratios.

paper (fig. 15) clearly indicates a straight-line trend as shown by the calculated least-squares line.

The analysis of variance is shown in table 5. The variance ratio,  $F$ , indicates that there is less than 1 chance in 100 that the ratio would be exceeded by random variation; that is, the variation of the peak-height ratios for all levels of concentration of calcite and dolomite is due to variation in the relative amount of calcite or dolomite. Thus question 1 is answered.

Interaction between calcite and dolomite ratios and the background minerals, though not directly tested, is not evident.

*Correlation coefficient and least-squares trend.*—The expression for determining the correlation coefficient,  $r$ , is

$$r = \frac{\sum xy - \frac{(\sum x)(\sum y)}{N}}{\left[ \frac{\sum x^2 - \frac{(\sum x)^2}{N}}{N} \right]^{\frac{1}{2}} \left[ \frac{\sum y^2 - \frac{(\sum y)^2}{N}}{N} \right]^{\frac{1}{2}}}$$

where  $x$  and  $y$  represent the percentage and peak-height ratios, respectively, and  $N$  is the number of ratios of each kind. The value for the correlation coefficient is 0.9541, which indicates a very high correlation between  $x$  and  $y$ . This provides an answer to question 2; the peak-height ratio is very useful as a measure of the ratio of calcite to dolomite.

TABLE 5.—*Analysis of variance of peak-height ratios for calcite and dolomite*

Source of variation	Number of mineral mixtures	Degrees of freedom	Formulas for sum of squares <sup>1</sup>	Sum of squares (SS)	Mean square <sup>2</sup> (MS)	Variance ratio <sup>3</sup> (F)
Calcite <sup>4</sup> .....	-----	3	$\left[ \frac{\sum_1^4 (\sum_2^4 x)^2}{4} \right]$	1.4611	0.4870	<sup>5</sup> 23.6
Dolomite <sup>4</sup> .....	-----	3	$\left[ \frac{\sum_1^4 (\sum_2^4 x)^2}{4} \right]$	1.5204	.5068	<sup>6</sup> 24.6
Remainder.....	-----	9	$[\sum x^2] - 1.5204 - 1.4611$	.1852	.0206	-----
Total.....	16	15	$[\sum_1^4 x^2]$	3.1667	.2111	-----

<sup>1</sup> Subtract correction term  $(\sum_1^4 x)^2/16$  from each formula.

<sup>2</sup> Determined by dividing the sum of squares by the degrees of freedom.

<sup>3</sup> Significant at 0.01 level of probability.

<sup>4</sup> Four levels of concentration—5, 20, 35, and 50 percent.

<sup>5</sup> Determined by dividing the mean square of calcite (0.4870) by that of the remainder (0.0206).

<sup>6</sup> Determined by dividing the mean square of dolomite (0.5068) by that of the remainder (0.0206).

### APPLICATION

An estimate of the ratio of calcite to dolomite in a bulk rock sample can be made with the use of figure 15. The value for the log of the peak-height ratio,  $y$ , is followed along the abscissa until the line of least squares,  $y = 0.3921 + 0.7885x$ , is intersected. The value,  $x$ , read on the abscissa at that point is the estimate of the log of the percentage ratio of calcite to dolomite in the rock.

### LITERATURE CITED

- DeKeyser, W. L. and Degueudre, L., 1950, Contribution à l'étude de la formation de la calcite, aragonite et vaterite: Soc. chim. Belgique Bull. 59, 40-71.
- Faivre, R., 1944, Studies, by X-ray diffraction and dilatometric analysis, of mixed carbonates of calcium and strontium and their transformations: Acad. Sci. [Paris] Comptes rendus, v., 219, 73-74.
- Krumbein, W. L., and Miller, R. L., 1953, Design of experiments for statistical analysis of geological data: Jour. Geology, v. 61, p. 510-532.
- Stolkowski, J., 1948, Quelques précisions sur l'analyse quantitative par les rayons de mélanges binaires et ternaires de carbonate de calcium anhydre: Acad. Sci. [Paris] Comptes rendus, v., 226, 933-934.
- Tennant, C. B., and Berger, R. W., 1957, X-ray determination of the dolomite-calcite ratio of a carbonate rock: Am. Mineralogist, v. 42, p. 23-29.